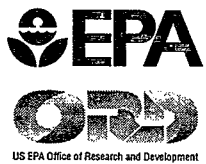


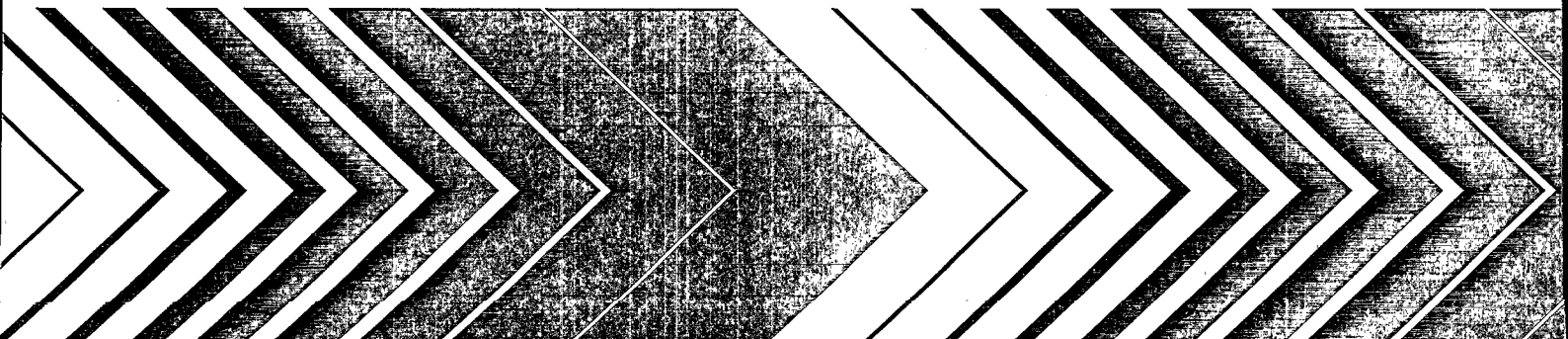
United States
Environmental Protection
Agency

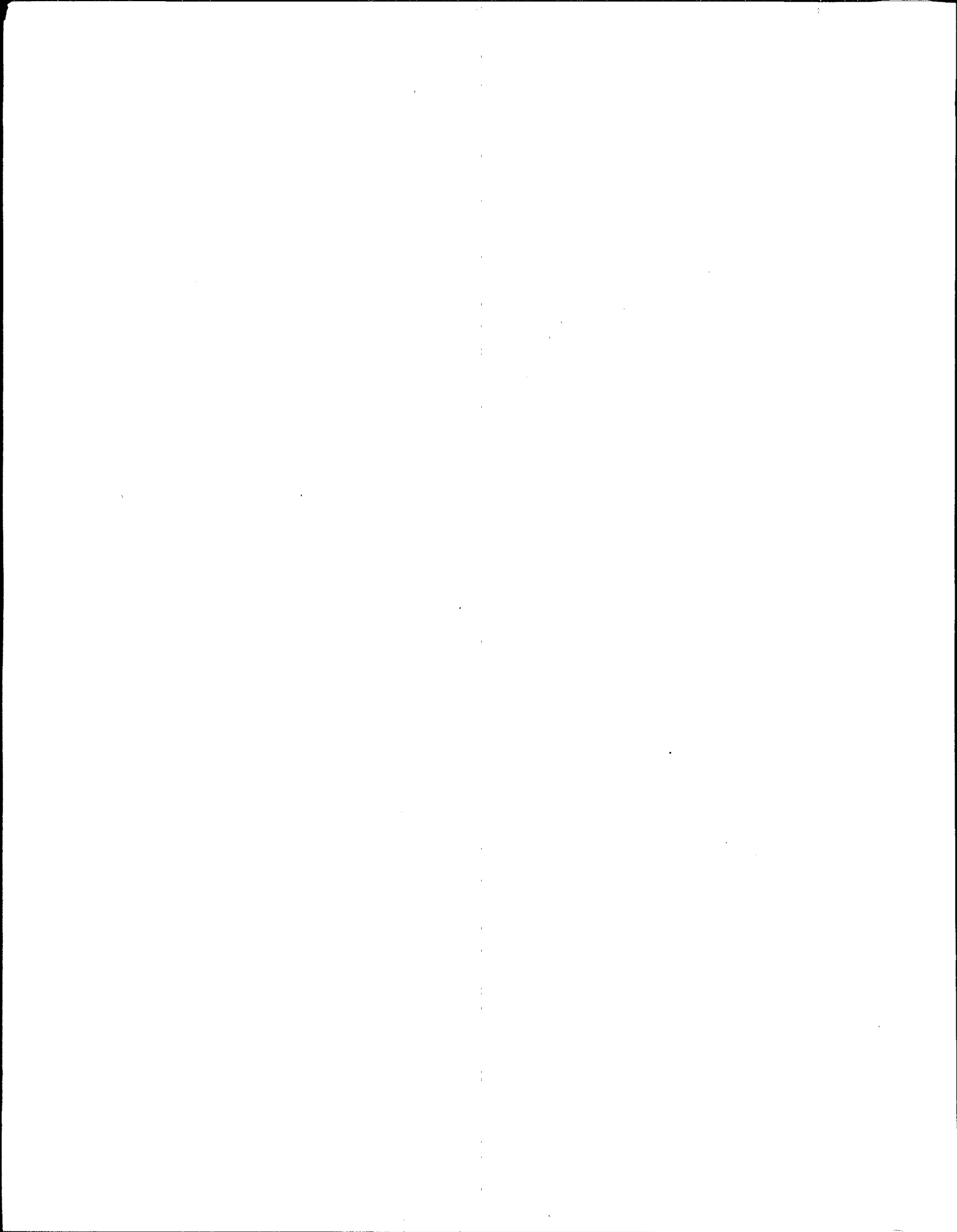
Office of Research and
Development
Washington DC 20460

EPA/600/R-00/096
October 2000



Volatilization Rates from Water to Indoor Air Phase II





EPA 600/R-00/096
October 2000

VOLATILIZATION RATES FROM WATER TO INDOOR AIR
PHASE II

National Center for Environmental Assessment—Washington Office
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460



Printed on Recycled Paper

DISCLAIMER

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Contaminated water can lead to volatilization of chemicals to residential indoor air. Previous research has focused on only one source (shower stalls) and has been limited to chemicals in which gas-phase resistance to mass transfer is of marginal significance. As a result, attempts to extrapolate chemical emissions from high-volatility chemicals to lower volatility chemicals, or to sources other than showers, have been difficult or impossible.

In this study two-phase dynamic mass balance models were developed for estimating chemical emissions from washing machines, dishwashers, and bathtubs. An existing model was adopted for showers only. Source- and chemical-specific mass transfer coefficients, as well as air exchange (ventilation) rates were estimated based on a series of experiments. These experiments were conducted using 5 tracer chemicals (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane) and 4 sources (showers, bathtubs, washing machines, and dishwashers). Each set of experiments led to the determination of chemical stripping efficiencies and mass transfer coefficients (overall, liquid-phase, gas-phase), and to an assessment of the importance of gas-phase resistance to mass transfer. Stripping efficiencies ranged from 6.3% to 80% for showers, 2.6% to 69% for bathtubs, 18% to 100% for dishwashers, and 3.8% to 100% for washing machines. Acetone and cyclohexane always defined the lower and upper bounds, respectively, of these ranges.

CONTENTS

List of Tables	viii
List of Figures	xi
Nomenclature and Abbreviations	xiii
Preface	xvi
Authors, Contributors, and Reviewers	xvii
Executive Summary	xix
1. Introduction	1-1
1.1. Problem Statement	1-1
1.2. Research Objectives	1-2
1.3. Scope of Research	1-2
1.4. Organization of Research Report	1-2
2. Model Development	2-1
2.1. Mass Transfer Theory	2-1
2.1.1. Chemical Stripping Efficiency	2-1
2.1.2. Mass Transfer Coefficients	2-2
2.2. Ideal Reactor Models	2-9
2.2.1. Plug Flow Reactor Model	2-9
2.2.2. Continuous-Flow Stirred-Tank Reactor Model	2-10
2.2.3. Batch Reactor Model	2-11
2.3. Source-Specific Mass Balance Models	2-12
2.3.1. Dishwasher Models	2-12
2.3.2. Washing Machine Models	2-16
2.3.2.1. Washing Machine Fill Cycle	2-16
2.3.2.2. Washing Machine Wash/Rinse Cycles	2-18
2.3.3. Shower Models	2-18
2.3.4. Bathtub Models	2-21
2.3.4.1. Bathtub Flow-Through Model	2-21
2.3.4.2. Bathtub Fill Model	2-21
2.3.4.3. Bathtub Surface Volatilization Model	2-21
2.4. Chemical Emission Models	2-22

CONTENTS (continued)

3. General Methodology	3-1
3.1. Source Chamber	3-1
3.2. Chemical Tracers	3-2
3.2.1. Physicochemical Properties	3-2
3.2.2. Chemical Tracer Addition	3-3
3.3. Chemical Sampling	3-4
3.3.1. Liquid-Phase Sampling	3-4
3.3.2. Gas-Phase Sampling	3-5
3.4. Sample Analyses	3-6
3.4.1. Liquid Sample Analysis	3-6
3.4.2. Liquid Standards	3-7
3.4.3. Gas Sample Analysis	3-9
3.4.4. Gas Standards	3-9
3.5. Quality Assurance Measures	3-11
3.5.1. Duplicate Samples	3-11
3.5.2. Replicate Experiments	3-12
3.5.3. Experimental Blanks	3-13
3.5.4. Method Detection Limit	3-13
3.6. Data Analysis	3-14
3.6.1. Chemical Stripping Efficiencies	3-15
3.6.2. Overall Mass Transfer Coefficients ($K_L A$)	3-15
3.6.3. Ratio of Gas-to-Liquid Phase Mass Transfer Coefficients	3-17
3.6.4. Liquid- and Gas-Phase Mass Transfer Coefficients	3-18
3.7. Factorial Analysis	3-18
3.8. Mass Closure Assessment	3-18
 4. Shower Stall Experiments	 4-1
4.1. Experimental System	4-1
4.2. Experimental Design	4-3
4.3. Source-Specific Methodology	4-4
4.3.1. Sample Schedule	4-4
4.3.2. Ventilation Rate	4-5
4.3.3. Parameter Estimation	4-5
4.4. Shower Results	4-5
4.4.1. Chemical Stripping Efficiencies	4-5

CONTENTS (continued)

4.4.2.	K_LA Values	4-17
4.4.3.	Liquid- and Gas-Phase Mass Transfer Coefficients	4-26
4.4.4.	Mass Closure	4-30
5.	Dishwasher Experiments	5-1
5.1.	Experimental System	5-1
5.2.	Experimental Design	5-2
5.3.	Source-Specific Methodology	5-3
5.3.1.	Sample Schedule	5-4
5.3.2.	Ventilation Rate	5-4
5.3.3.	Parameter Estimation	5-4
5.4.	Dishwasher Results	5-7
5.4.1.	Ventilation Rates	5-7
5.4.2.	Chemical Stripping Efficiencies	5-8
5.4.3.	K_LA Values	5-12
5.4.4.	Liquid- and Gas-Phase Mass Transfer Coefficients	5-19
5.4.5.	Mass Closure	5-20
6.	Washing Machine Experiments	6-1
6.1.	Fill Cycle Experiments	6-1
6.1.1.	Experimental System	6-1
6.1.2.	Experimental Design	6-3
6.1.3.	Source-Specific Methodology	6-3
6.1.3.1.	Sample Schedule	6-4
6.1.3.2.	Ventilation Rates	6-5
6.1.3.3.	Parameter Estimation	6-6
6.1.4.	Fill Cycle Results	6-7
6.1.4.1.	Ventilation Rates	6-8
6.1.4.2.	Chemical Stripping Efficiencies	6-9
6.1.4.3.	K_LA Values	6-11
6.1.4.4.	Liquid- and Gas-Phase Mass Transfer Coefficients	6-12
6.1.4.5.	Mass Closure	6-13
6.2.	Wash/Rinse Cycle Experiments	6-14
6.2.1.	Experimental System	6-14
6.2.2.	Experimental Design	6-15

CONTENTS (continued)

6.2.3. Source-Specific Methodology	6-15
6.2.3.1. Sample Schedule	6-16
6.2.3.2. Ventilation Rates	6-16
6.2.3.3. Parameter Estimation	6-16
6.2.4. Wash/Rinse Cycle Results	6-17
6.2.4.1. Ventilation Rates	6-18
6.2.4.2. Chemical Stripping Efficiencies	6-20
6.2.4.3. K_LA Values	6-31
6.2.4.4. Liquid- and Gas-Phase Mass Transfer Coefficients	6-42
6.2.4.5. Mass Closure	6-45
 7. Bathtub Experiments	 7-1
7.1. Bathtub Flow-Through Experiments	7-1
7.1.1. Experimental System	7-1
7.1.2. Experimental Design	7-1
7.1.3. Source-Specific Methodology	7-1
7.1.3.1. Sample Schedule	7-1
7.1.3.2. Ventilation Rate	7-2
7.1.3.3. Parameter Estimation	7-2
7.1.4. Bathtub Flow-Through Results	7-3
7.1.4.1. Chemical Stripping Efficiencies	7-3
7.1.4.2. K_LA Values	7-5
7.1.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients	7-7
7.1.4.4. Mass Closure	7-8
7.2. Bathtub Fill Experiments	7-9
7.2.1. Experimental System	7-9
7.2.2. Experimental Design	7-9
7.2.3. Source-Specific Methodology	7-9
7.2.3.1. Sample Schedule	7-9
7.2.3.2. Ventilation Rates	7-11
7.2.3.3. Parameter Estimation	7-11
7.2.4. Bathtub Fill Results	7-11
7.2.4.1. Chemical Stripping Efficiencies	7-11
7.2.4.2. Values	7-13
7.2.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients	7-13

CONTENTS (continued)

7.2.4.4. Mass Closure	7-13
7.3. Surface Volatilization Experiments	7-14
7.3.1. Experimental System	7-14
7.3.2. Experimental Design	7-15
7.3.3. Source-Specific Methodology	7-15
7.3.3.1. Sample Schedule	7-15
7.3.3.2. Ventilation Rates	7-15
7.3.3.3. Parameter Estimation	7-15
7.3.4. Bathtub Surface Volatilization Results	7-16
7.3.4.1. Chemical Stripping Efficiencies	7-17
7.3.4.2. $K_L A$ Values	7-18
7.3.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients	7-19
7.3.4.4. Mass Closure	7-19
8. Model Applications	8-1
8.1. Shower Model Application	8-1
8.2. Dishwasher Model Application	8-7
8.3. Washing Machine Model Application	8-13
8.4. Bathtub Model Application	8-19
9. Summary and Conclusions	9-1
9.1. Summary	9-1
9.2. Conclusions: General	9-3
9.3. Conclusions: Showers	9-4
9.4. Conclusions: Dishwashers	9-5
9.5. Conclusions: Washing Machines	9-5
9.6. Conclusions: Bathtubs	9-6
9.7. Recommendations for Future Research	9-7
10. References	10-1
Appendix: Chemical Volatilization Database	A-1

LIST OF TABLES

3-1	Summary of physicochemical properties for selected chemical tracers	3-2
3-2	Duplicate sample results	3-11
3-3	Replicate sample results	3-12
3-4	Replicate sample results excluding replicate experiments associated with filling	3-13
3-5	Method detection limits (MDLs) for liquid and gas samples	3-14
4-1	Shower experiment operating conditions	4-6
4-2	Acetone stripping efficiencies for experimental shower	4-7
4-3	Ethyl acetate stripping efficiencies for experimental shower	4-7
4-4	Toluene stripping efficiencies for experimental shower	4-8
4-5	Ethylbenzene stripping efficiencies for experimental shower	4-8
4-6	Cyclohexane stripping efficiencies for experimental shower	4-9
4-7	Acetone K_LA values for experimental shower	4-18
4-8	Ethyl acetate K_LA values for experimental shower	4-18
4-9	Toluene K_LA values for experimental shower	4-19
4-10	Ethylbenzene K_LA values for experimental shower	4-19
4-11	Cyclohexane K_LA values for experimental shower	4-20
4-12	Liquid- and gas-phase mass transfer coefficients for shower experiments	4-27
5-1	Dishwasher experimental operating conditions	5-7
5-2	Dishwasher ventilation rate experimental results	5-9
5-3	Chemical stripping efficiencies (η) for experimental dishwasher	5-10
5-4	Acetone K_LA values for dishwasher experiments	5-13
5-5	Toluene K_LA values for dishwasher experiments	5-13
5-6	Ethylbenzene K_LA values for dishwasher experiments	5-14
5-7	Cyclohexane K_LA values for dishwasher experiments	5-14
6-1	Washing machine fill cycle experimental conditions	6-8
6-2	Washing machine fill cycle ventilation rates	6-9
6-3	Chemical stripping efficiencies (η) for washing machine fill cycles	6-10
6-4	Values of K_LA for washing machine fill cycles	6-12
6-5	Liquid- and gas-phase mass transfer coefficients for washing machine fill cycle experiments	6-13
6-6	Washing machine wash/rinse cycle experimental operating conditions	6-18
6-7	Ventilation rate experimental results	6-19
6-8	Acetone stripping efficiencies for washing machine wash/rinse cycle—Factorial #1 ..	6-20
6-9	Acetone stripping efficiencies for washing machine wash/rinse cycle—Factorial #2 ..	6-21

LIST OF TABLES (continued)

6-10 Ethyl acetate stripping efficiencies for washing machine wash/rinse cycle— Factorial #2.	6-21
6-11 Toluene stripping efficiencies for washing machine wash/rinse cycle—Factorial #1 ...	6-22
6-12 Toluene stripping efficiencies for washing machine wash/rinse cycle—Factorial #2 ..	6-22
6-13 Ethylbenzene stripping efficiencies for washing machine wash/rinse cycle— Factorial #1	6-23
6-14 Ethylbenzene stripping efficiencies for washing machine wash/rinse cycle— Factorial #2	6-23
6-15 Cyclohexane stripping efficiencies for washing machine wash/rinse cycle— Factorial #1	6-24
6-16 Cyclohexane stripping efficiencies for washing machine wash/rinse cycle— Factorial #2	6-24
6-17 Acetone K_LA values for washing machine wash/rinse cycle—Factorial #1	6-32
6-18 Acetone K_LA values for washing machine wash/rinse cycle—Factorial #2	6-32
6-19 Ethyl acetate K_LA values for washing machine wash/rinse cycle—Factorial #2	6-33
6-20 Toluene K_LA values for washing machine wash/rinse cycle—Factorial #1	6-33
6-21 Toluene K_LA values for washing machine wash/rinse cycle—Factorial #2	6-34
6-22 Ethylbenzene K_LA values for washing machine wash/rinse cycle—Factorial #1	6-34
6-23 Ethylbenzene K_LA values for washing machine wash/rinse cycle—Factorial #2	6-35
6-24 Cyclohexane K_LA values for washing machine wash/rinse cycle—Factorial #1	6-35
6-25 Cyclohexane K_LA values for washing machine wash/rinse cycle—Factorial #2	6-36
6-26 Liquid- and gas-phase mass transfer coefficients for washing machine wash/rinse cycle experiments—Factorial #1	6-46
6-27 Liquid- and gas-phase mass transfer coefficients for washing machine wash/rinse cycle experiments—Factorial #2	6-47
7-1 Bathtub flow-through operating conditions	7-3
7-2 Chemical stripping efficiencies (η) for experimental bathtub flow-through experiments	7-4
7-3 Values of K_LA for bathtub flow-through experiments	7-5
7-4 Liquid- and gas-phase mass transfer coefficients for bathtub flow-through experiments.	7-7
7-5 Bathtub (fill) operating conditions	7-12
7-6 Chemical stripping efficiencies (η) for bathtub (fill) experiments	7-12
7-7 Values of K_LA for bathtub (fill) experiments	7-13
7-8 Liquid- and gas-phase mass transfer coefficients for bathtub (fill) experiments	7-14

LIST OF TABLES (continued)

7-9	Bathtub surface volatilization operating conditions	7-17
7-10	Chemical stripping efficiencies for bathtub surface volatilization experiments	7-18
7-11	Values of $K_L A$ for bathtub surface volatilization experiments	7-18
7-12	Liquid- and gas-phase mass transfer coefficients for bathtub surface volatilization experiments	7-20
8-1	Comparison of the three chemicals used in model applications	8-2
9-1	Summary of experimental stripping efficiencies and k_g/k_l	9-2

LIST OF FIGURES

2-1	Plug flow reactor	2-10
2-2	Continuous-flow stirred-tank reactor	2-11
2-3	Batch reactor	2-11
2-4	Dishwasher model	2-13
2-5	Washing machine fill cycle model	2-17
2-6	Washing machine wash/rinse cycle model	2-18
2-7	Shower model	2-19
2-8	Bathtub flow-through model	2-22
2-9	Bathtub fill model	2-22
2-10	Bathtub surface volatilization model	2-23
3-1	Gas sampling experimental set up	3-6
3-2	Liquid-phase sample chromatogram	3-7
3-3	Liquid-phase calibration curve for ethylbenzene	3-8
3-4	Gas sample chromatogram	3-10
3-5	Gas-phase calibration curve for acetone	3-10
3-6	Matrix format used to determine k_g/k_l	3-19
4-1	Shower experimental system	4-2
4-2	Shower factorial experimental design	4-3
	Relationship between Henry's law constant and average stripping efficiency	4-16
4-4	Acetone experimental data for Experiment 7	4-20
4-5	Ethyl acetate experimental data for Experiment 7	4-22
4-6	Toluene experimental data for Experiment 7	4-23
4-7	Ethylbenzene experimental data for Experiment 7	4-24
4-8	Cyclohexane experimental data for Experiment 7	4-25
4-9	Resistances to mass transfer for each chemical in Experiment 7	4-29
5-1	Dishwasher experimental system	5-2
5-2	Factorial experimental design for dishwasher experiments	5-3
5-3	Isobutylene decay due to ventilation for Experiment 18	5-9
5-4	Comparison of measured C_g/C_l predicted Henry's law constant for acetone	5-16
5-5	Toluene concentrations for Experiment 8	5-17
5-6	Amplification of Figure 30 to illustrate approach to equilibrium conditions for toluene	5-18
5-7	Ethylbenzene concentrations for Experiment 8	5-19
5-8	Cyclohexane concentrations for Experiment 8	5-20

LIST OF FIGURES (continued)

6-1	Washing machine fill cycle experimental system	6-2
6-2	Isobutylene decay due to ventilation for Experiment 13	6-9
6-3	Wash/rinse cycle experimental system	6-14
6-4	Wash/rinse cycle factorial experimental design	6-15
6-5	Isobutylene decay due to ventilation for Experiment 8	6-20
6-6	Acetone concentrations for Experiment 6	6-37
6-7	Amplification of Figure 6-6 for acetone gas-phase data	6-38
6-8	Toluene concentrations for Experiment 6	6-40
6-9	Magnification of Figure 6-8 to illustrate toluene's gas-phase concentration over time	6-40
6-10	Ethylbenzene concentrations for Experiment 6	6-42
6-11	Cyclohexane concentrations for Experiment 6	6-43
6-12	Liquid- and gas-phase resistances to mass transfer for Experiment 6	6-44
7-1	Bathtub flow-through experimental system	7-2
7-2	Toluene experimental data for Experiment 4 replicate	7-6
7-3	Resistances to mass transfer for each chemical in Experiment 2	7-8
7-4	Bathtub fill experimental system	7-10
7-5	Toluene experimental data for Experiment 4 replicate	7-19
8-1	Mass emission rates for three chemicals for example shower event	8-2
8-2	Mass emission rates for three chemicals for example dishwasher event	8-11
8-3	Amplification of Figure 52 to show methyl ethyl ketone mass emission rate	8-12
8-4	Mass emission rates for three chemicals for example washing machine event	8-18
8-5	Mass emission rates for three chemicals for example bathtub event	8-20

NOMENCLATURE AND ABBREVIATIONS¹

A	interfacial surface area between water and adjacent air (L^2)
ACH	air changes per hour
ΔA	differential ¹ area (L^2)
C	chemical concentration (M/L^3)
C_{expt}	experimentally measured liquid- and gas-phase concentrations (M/L^3)
C_g	chemical concentration in air adjacent to water (M/L^3)
$C_{g,\text{in}}$	inlet concentration of contaminant in air (M/L^3)
$C_{g,0}$	initial chemical concentration in gas volume (M/L^3)
$C_{g,t}$	chemical concentration in air at any time t (M/L^3)
C_{in}	inlet chemical concentration (M/L^3)
C_l	chemical concentration in water (M/L^3)
$C_{l,\text{end}}$	final chemical concentration in water (M/L^3)
$C_{l,\text{in}}$	inlet chemical concentration in water (M/L^3)
$C_{l,\text{out}}$	outlet concentration of contaminant in water (M/L^3)
$C_{l,0}$	initial chemical concentration in water (M/L^3)
C_m	mathematically predicted liquid- and gas-phase concentrations (M/L^3)
CFSTR	continuous flow stirred tank reactor
cosh	hyperbolic cosine
coth	hyperbolic cotangent
D_g	molecular diffusion coefficient for a chemical in air (L^2/T)
D_{gi}	molecular diffusion coefficient for chemical i in air (L^2/T)
D_{gj}	molecular diffusion coefficient for chemical j in air (L^2/T)
D_l	molecular diffusion coefficient for a contaminant in water (L^2/T)
D_{li}	molecular diffusion coefficient for chemical i in water (L^2/T)
D_{lj}	molecular diffusion coefficient for chemical j in water (L^2/T)
DBCM	dibromochloromethane
DBCP	1,2-dibromo-3-chloropropane
E_{chem}	chemical mass emission rate (M/T)
FID	flame ionization detector
GC	gas chromatography

¹ Note: Terms in parentheses denote units; M corresponds to mass; L corresponds to length; T corresponds to time; ($^{\circ}$) corresponds to temperature; dimensionless values are denoted as (-).

NOMENCLATURE AND ABBREVIATIONS (continued)

H_c	Henry's law constant ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
$H_{c,i}$	Henry's law constant for chemical i ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
$H_{c,j}$	Henry's law constant for chemical j ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
$H_{c,T}$	Henry's law constant at experimental temperature ($L^3_{\text{gas}}/L^3_{\text{liq}}$)
ID	inside diameter (L)
k_g	gas-phase mass transfer coefficient (L/T)
$k_{g,i}$	gas-phase mass transfer coefficient for chemical i (L/T)
$k_{g,j}$	gas-phase mass transfer coefficient for chemical j (L/T)
K_L	overall mass transfer coefficient for contaminant of interest (L/T)
k_l	liquid-phase mass transfer coefficient (L/T)
$K_{L,i}$	overall mass transfer coefficient for chemical i (L/T)
$k_{l,i}$	liquid-phase mass transfer coefficient for chemical i (L/T)
$K_{L,j}$	overall mass transfer coefficient for chemical j (L/T)
$k_{l,j}$	liquid-phase mass transfer coefficient for chemical j (L/T)
m_c	degree of mass closure (-)
MDL	method detection limit
MEK	methyl ethyl ketone
n_1	power constant for ratio of liquid-phase diffusion coefficients (-)
n_2	power constant for ratio of gas-phase diffusion coefficients (-)
OD	outside diameter (L)
P	perimeter (L)
pFR	plug flow reactor
Pv	vapor pressure (L Hg)
Q	volumetric flowrate (L^3/T)
Q_g	gas flowrate (L^3/T)
Q_{in}	inlet volumetric flowrate (L^3/T)
Q_l	liquid flowrate (L^3/T)
Q_{out}	outlet volumetric flowrate (L^3/T)
r_A	area reaction rate ($M/L^2 \cdot T$)
r_g	rate of surface renewal for the gas side of the interface (1/T)
r_l	rate of surface renewal for the liquid side of the interface (1/T)
r_v	volume reaction rate ($M/L^3 \cdot T$)
sinh	hyperbolic sine
s_r	standard deviation of replicate analyses

NOMENCLATURE AND ABBREVIATIONS (continued)

t	time (T)
T	temperature ($^{\circ}\text{C}$)
T_b	boiling point ($^{\circ}\text{C}$)
TCE	trichloroethene
TKE	total kinetic energy
V	volume (L^3)
ΔV	differential volume (L^3)
V_g	local volume of air (L^3)
V_l	local volume of water (L^3)
z	direction of flow
δ_g	thickness of a hypothetical gas film adjacent to the interface and through which contaminant transport is solely by molecular diffusion (L)
δ_l	thickness of a hypothetical liquid film adjacent to the interface and through which contaminant transport is solely by molecular diffusion (L)
η	chemical stripping efficiency (-)
ρ	density (M/L^3)
Ψ_g	gas-phase mass transfer relational coefficient (-)
Ψ_l	liquid-phase mass transfer relational coefficient (-)
Ψ_m	overall mass transfer relational coefficient (-)

PREFACE

This report was prepared under the direction of the National Center for Environmental Assessment (NCEA) of EPA's Office of Research and Development (ORD). The purpose of this report is to provide a methodology for estimating chemical emissions from washing machines, dishwashers, showers, and bathtubs. The methodology presented in this report was derived from volatilization experiments conducted by The University of Texas at Austin under a Cooperative Agreement with NCEA. The results of these experiments are included in the report.

The report was submitted in fulfillment of Cooperative Agreement No. CR 824228-01 and covers the period from June 1, 1995 to August 31, 1997, and work was completed as of August 31, 1997.

AUTHORS, CONTRIBUTORS, AND REVIEWERS

This report was prepared under Cooperative Agreement No. CR 824228-01 between The University of Texas at Austin and the National Center for Environmental Assessment (NCEA), Office of Research and Development. Jacqueline Moya was responsible for the overall coordination, direction, and technical assistance.

AUTHORS

Cynthia Howard-Reed
formerly Graduate Research Assistant with The University of Texas at Austin
presently with the Indoor Air Quality Group at the National Institute of Standards and Technology (NIST)

Richard L. Corsi
Principal Investigator
Environmental and Water Resources Engineering Program
The University of Texas at Austin

REVIEWERS

The following individuals have reviewed this report and provided valuable comments:

Environmental Protection Agency Reviewers

Jacqueline Moya
Nancy Chiu
Lance Wallace

External Reviewers

John Little
Associate Professor
Civil and Environmental Engineering
Virginia Tech
Blacksburg, VA

Nicholas J. Giardino
Toxicologist
Brooks AFB, Texas

AUTHORS, CONTRIBUTORS, AND REVIEWERS (continued)

ACKNOWLEDGMENTS

The authors wish to thank EPA Project Officer Jacqueline Moya for her general guidance and enthusiasm regarding this project. The authors also wish to acknowledge Albert Chung, Jennifer Pettibon, Javier Ramirez, Tony Smith, and Ross Strader, undergraduate students at The University of Texas at Austin, for their assistance during experiments.

EXECUTIVE SUMMARY

Contaminated water can lead to volatilization of chemicals to residential indoor air. Previous research has focused on only one source (shower stalls) and has been limited to chemicals in which gas-phase resistance to mass transfer is of marginal significance. As a result, attempts to extrapolate chemical emissions from high-volatility chemicals to lower volatility chemicals, or to sources other than showers, have been difficult or impossible.

In this study two-phase dynamic mass balance models were developed for estimating chemical emissions from washing machines, dishwashers, and bathtubs. An existing model was adopted for showers only. The mass transfer theory and derivations of these models are further described in chapter 2 of this report. Source- and chemical-specific mass transfer coefficients, as well as air exchange (ventilation) rates were estimated based on a series of experiments. These experiments were conducted using 5 tracer chemicals (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane) and 4 sources (showers, bathtubs, washing machines, and dishwashers). Each set of experiments led to the determination of chemical stripping efficiencies and mass transfer coefficients (overall, liquid-phase, gas-phase), and to an assessment of the importance of gas-phase resistance to mass transfer.

A set of protocols for estimating emission rates for chemicals other than those used in this study was defined for each of the four sources. Example applications are provided and illustrate the dynamic behavior of emissions and importance of chemical properties on such emissions. The experimental mass transfer coefficients, air exchange rates and protocols described in this report can be used as direct input values or to estimate reasonable input values for the reported emission models.

Stripping efficiencies ranged from 6.3% to 80% for showers, 2.6% to 69% for bathtubs, 18% to 100% for dishwashers, and 3.8% to 100% for washing machines. Acetone and cyclohexane always defined the lower and upper bounds, respectively, of these ranges.

The findings of this study lead to several conclusions. A detailed discussion of conclusions is presented in chapter 9. Some of the most significant conclusions are summarized below.

- System operating conditions can have a significant effect on chemical emissions. In particular, chemical stripping efficiencies for washing machines were observed to be highly sensitive to system operating conditions.
- Water temperature was an important variable that affected stripping efficiencies and mass transfer coefficients for all sources.

- Chemical stripping efficiencies increase as Henry's law constant increases for lower-volatility chemicals. However, with the exception of the fill-cycle of bathtubs, chemical stripping efficiencies are relatively insensitive to Henry's law constant for chemicals with constants greater than that of toluene.
- Failure to account for gas-phase resistance to mass transfer can lead to significant overestimates of chemical volatilization to indoor air. This is particularly true for lower-volatility chemicals or those sources with low values of gas- to liquid-phase mass transfer coefficients (k_g/k_l), e.g., washing machines.
- Results for shower experiments were reasonably consistent with those reported by other researchers with stripping efficiencies ranging from 60% to 80% for chemicals with Henry's law constant equal or greater than that of toluene.
- Gas-phase concentrations were homogeneous throughout the shower stall demonstrating that the frequent assumption of a well-mixed system is reasonably accurate.
- Dishwashers were determined to be very effective at removing chemicals from water to air, with low but continuous emissions during operation and significant storage within the dishwasher headspace. The most significant release of chemicals to indoor air would occur if the dishwasher door is opened immediately after use.
- Washing machines during the rinse cycle with hot water and low clothes loading resulted in stripping efficiencies that approached 100% for chemicals with Henry's law constant greater than toluene.
- Bathtubs may be more significant than showers with respect to human exposure to chemicals dissolved in water because of longer exposure times.

1. INTRODUCTION

1.1. PROBLEM STATEMENT

Current Federal drinking water (chemical) standards are primarily based on associated ingestion exposure. However, other exposure routes—inhale and dermal contact—may be as or more important in terms of human health risk (McKone, 1987). Contaminated tap water can enter a home through several sources, including showers, bathtubs, washbasins, dishwashers, and washing machines. For each of these sources, chemicals have the potential to volatilize to indoor air and thus provide an inhalation risk to humans. Previous studies on volatilization of chemicals from drinking water to indoor air have been narrow in focus and have failed to close several "knowledge gaps." These knowledge gaps currently hinder accurate inhalation exposure assessments.

To date, research on volatilization of chemicals from drinking water has focused on one household source, showers. Despite the relatively large number of shower experiments, previous studies have focused on stripping efficiencies for a narrow range of chemicals, primarily radon (Rn-222), trichloroethene (TCE), and chloroform (CHCl₃). Thus, current methods for estimating inhalation exposure related to contaminated tap water are based on simplifying assumptions and/or extrapolation techniques that fail to capture the mechanistic behavior of the volatilization process. For example, these extrapolation techniques are limited by the lack of specific mass transfer coefficients for chemicals that vary significantly in their volatility. Thus, there is an important need to expand current knowledge about chemical volatilization from tap water.

This research project was completed in two phases. The first phase was dedicated to an extensive literature search to establish the current knowledge base regarding mass transfer of volatile chemicals from household water sources. This literature search has been documented elsewhere (Corsi et al., 1996). Results of Phase I led to the conclusion that there was a significant need for experiments to estimate chemical volatilization for all household consumptive water uses. Four sources were chosen for further study (Phase II). The four sources were showers, dishwashers, washing machines, and bathtubs, all of which were chosen based on predicted significance of chemical emissions.

A series of experiments was completed to determine chemical volatilization rates for each of the four sources. Results from this work have been used to develop and evaluate improvements

to existing extrapolation models for relating rates of volatilization and mass transfer coefficients between chemicals.

1.2. RESEARCH OBJECTIVES

The research objectives of Phase II were as follows:

1. Use a series of well-designed laboratory experiments to expand the general knowledge base associated with chemical volatilization to indoor air.
2. Develop and evaluate improvements to existing models based on empirical and mechanistic accounting for source operating conditions and contaminant physicochemical properties.
3. Compile and organize these experimental data in a database that may be easily used by regulators, consultants, academics, and others.

1.3. SCOPE OF RESEARCH

A two-phase mass balance model was developed for each of the four sources described in Section 1.1. Laboratory experiments were designed such that the mass balance model was solved to back-calculate mass transfer coefficients for each chemical and source. These experiments were completed using a water supply spiked with a cocktail of chemicals representing a wide range of Henry's law constants. For each source, chemical stripping efficiencies and mass transfer coefficients were determined for several applicable operating conditions (water temperature, liquid flowrate, presence of detergent, etc.). A total of 113 mass transfer and air exchange rate experiments were completed.

1.4. ORGANIZATION OF RESEARCH REPORT

Mass balance models used for each experimental source are presented in Section 2. General experimental methodologies and analytical techniques are described in Section 3. Sections 4 through 7 include presentations of each experimental system, experimental design, source-specific methodologies, and experimental results for the respective sources. A model application for each source is presented in Section 8. Conclusions and recommendations based on this research are presented in Section 9. All applicable references are included in Section 10. Finally, the data from the experimental database are provided in the Appendix.

2. MODEL DEVELOPMENT

The first step in studying each experimental source was to develop a two-phase mass balance model describing the rate at which a chemical enters, leaves, or accumulates within the system. A key component of each source model was the rate at which a chemical leaves the liquid phase and enters the gas phase. This volatilization rate may be described in terms of a stripping efficiency or mass transfer coefficient. To determine the volatilization rate for a source, a separate mass balance was completed on each phase. By simultaneously solving the respective differential equations, the source-specific chemical volatilization rate was predicted.

This section is divided into four parts. Section 2.1 involves the theory of mass transfer and important mass transfer parameters. Section 2.2 presents the different mass balance models used for ideal reactors. Section 2.3 describes the mass balance models developed for each experimental system. Finally, Section 2.4 describes the chemical emission models associated with each source.

2.1. MASS TRANSFER THEORY

Although the operation of each household tap water source is very different, a similar group of mass transfer parameters may be applied to characterize the volatilization of chemicals. These parameters include chemical stripping efficiency, mass transfer coefficients (overall, liquid-phase, and gas-phase), and the ratio of overall mass transfer coefficients for any two contaminants. Each of these values is discussed in this section.

2.1.1. Chemical Stripping Efficiency

The stripping efficiency of a specific chemical for a flow-through system with a constant volumetric flowrate of water and no reactions is defined as:

$$\eta = 1 - \frac{C_{l,out}}{C_{l,in}} \quad (2-1)$$

where

- η = stripping efficiency (fractional)
- $C_{l,out}$ = outlet chemical concentration in water (M/L³)
- $C_{l,in}$ = inlet chemical concentration in water (M/L³).

Similarly, the stripping efficiency of a specific chemical for a batch system with a constant volume of water and no reaction is defined as:

$$\eta = 1 - \frac{C_{l,end}}{C_{l,0}} \quad (2-2)$$

where

- η = stripping efficiency (fractional)
- $C_{l,end}$ = final chemical concentration in water (M/L³)
- $C_{l,0}$ = initial chemical concentration in water (M/L³).

In general, a stripping efficiency requires measurement of the inlet liquid concentration to the system of interest and measurement of the outlet liquid concentration at the system's drain. Stripping efficiency values are influenced by several factors, including chemical properties (e.g., Henry's law constant [H_c]), temperature, nozzle type, liquid flowrate, gas flowrate, and presence of a person, detergent, clothes, and dishes (depending on the type of source).

2.1.2. Mass Transfer Coefficients

Each household source is characterized by a unique combination of mass transfer mechanisms that affect chemical volatilization rates. These mechanisms can include a falling film, (e.g., the jet associated with a faucet), spray droplets (e.g., in showers or dishwashers), splashing at surfaces (e.g., during the filling of a washing machine), and entrained air bubbles (e.g., when a faucet jet impacts an underlying basin). When two or more of these mechanisms are important, it is often difficult or impossible to determine separate mass transfer coefficients. It is common to "lump" the effects of multiple mass transfer mechanisms into a single overall mass transfer coefficient, K_L . The resulting equation for local rate of change of mass in the liquid phase associated only with volatilization is:

$$\eta = 1 - \frac{C_{1,out}}{C_{1,in}} \quad (2-3)$$

where

- C_1 = chemical concentration in water (M/L³)
- V_1 = local volume of water (L³)
- t = time (T)
- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- C_g = contaminant concentration in air adjacent to water (M/L³)
- H_c = Henry's law constant for chemical of interest (L³_{liq}/L³_{gas})

A = interfacial surface area between water and adjacent air (L^2).

For a dilute aqueous solution, the Henry's law constant for a specific chemical is defined as the ratio of chemical concentration in air to that in water at equilibrium. Values of Henry's law constant are dependent on chemical structure and water temperature. For most volatile organic compounds, the Henry's law constant can be approximated closely as the ratio of chemical vapor pressure to solubility in water. As such, a chemical (e.g., acetone) may be considered relatively volatile in its pure state (high vapor pressure) but also relatively nonvolatile when dissolved in water (miscible in water). The term $(C_l - C_g/H_c)$ is the concentration driving force between the liquid and gas phases. As the difference between C_l and C_g/H_c decreases, the system approaches chemical equilibrium.

In accordance with two-film theory (Lewis and Whitman, 1924), the overall mass transfer coefficient can be expressed as:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g \cdot H_c} \quad (2-4)$$

where

- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- k_l = liquid-phase mass transfer coefficient (L/T)
- k_g = gas-phase mass transfer coefficient (L/T)
- H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas}).

The term $1/K_L$ is referred to as an overall resistance to mass transfer. The term $1/k_l$ is referred to as liquid-phase resistance to mass transfer, and $1/(k_g \cdot H_c)$ is referred to as gas-phase resistance to mass transfer. For $k_g \cdot H_c \gg k_l$, gas-phase resistance to mass transfer is small and the overall mass transfer coefficient is approximately equal to the liquid-phase mass transfer coefficient. This condition is generally true for highly volatile compounds such as radon.

It is often difficult to separate mass transfer coefficients and the interfacial area (A) over which mass transfer occurs. This is particularly true for sources without well-defined or quiescent surfaces, for example, most indoor consumptive water uses. However, by dividing each term by $1/A$, Equation 2-4 can be effectively rewritten as:

$$\frac{1}{K_L A} = \frac{1}{k_l A} + \frac{1}{k_g A \cdot H_c} \quad (2-5)$$

where

- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- A = interfacial surface area between water and adjacent air (L^2)
- k_l = liquid-phase mass transfer coefficient (L/T)
- k_g = gas-phase mass transfer coefficient (L/T)
- H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas}).

In accordance with two-film theory (Lewis and Whitman, 1924), liquid- and gas-phase mass transfer coefficients are related to chemical properties and fluid flow conditions as follows:

$$k_l = \frac{D_l}{\delta_l} \quad (2-6)$$

$$k_g = \frac{D_g}{\delta_g} \quad (2-7)$$

where

- k_l = liquid-phase mass transfer coefficient (L/T)
- k_g = gas-phase mass transfer coefficient (L/T)
- D_l = molecular diffusion coefficient for a chemical in water (L^2/T)
- D_g = molecular diffusion coefficient for a chemical in air (L^2/T)
- δ_l = thickness of a hypothetical liquid film adjacent to the interface and through which chemical transport is solely by molecular diffusion (L)
- δ_g = thickness of a hypothetical gas film adjacent to the interface and through which chemical transport is solely by molecular diffusion (L).

Molecular diffusion coefficients vary to some extent between volatile chemicals and are a function of fluid temperature. The hypothetical film thicknesses are assumed to be a function of the extent of turbulent kinetic energy and subsequent mixing on either side of the interface, decreasing in width with an increase in turbulent kinetic energy. For dilute aqueous solutions, the film thicknesses are assumed to be independent of chemical concentrations.

For penetration theory (Higbie, 1935) and surface renewal theory (Danckwerts, 1951), liquid- and gas-phase mass transfer coefficients are predicted to be proportional to the product of molecular diffusion coefficients and surface renewal rates according to:

$$k_l \propto (D_l \cdot r_l)^{0.5} \quad (2-8)$$

$$k_g \propto (D_g \cdot r_g)^{0.5} \quad (2-9)$$

where

- k_l = liquid-phase mass transfer coefficient (L/T)
- k_g = gas-phase mass transfer coefficient (L/T)
- D_l = molecular diffusion coefficient for a chemical in water (L^2/T)
- D_g = molecular diffusion coefficient for a chemical in air (L^2/T)
- r_l = rate of surface renewal for the liquid side of the interface (1/T)
- r_g = rate of surface renewal for the gas side of the interface (1/T).

The hypothetical surface renewal rates are assumed to be independent of contaminant concentrations for dilute aqueous solutions. They are assumed to increase as turbulent kinetic energy in the bulk fluid increases.

Finally, Dobbins (1956) developed a theory (film-penetration theory) that incorporates the fundamental principles of both two-film and penetration theories. Corresponding relationships for k_l and k_g are:

$$k_l = (D_l r_l)^{\frac{1}{2}} \coth \left(\frac{r_l \delta_l^2}{D_l} \right)^{\frac{1}{2}} \quad (2-10)$$

$$k_g = (D_g r_g)^{\frac{1}{2}} \coth \left(\frac{r_g \delta_g^2}{D_g} \right)^{\frac{1}{2}} \quad (2-11)$$

where

- k_l = liquid-phase mass transfer coefficient (L/T)
- k_g = gas-phase mass transfer coefficient (L/T)
- D_l = molecular diffusion coefficient for a chemical in water (L^2/T)
- D_g = molecular diffusion coefficient for a chemical in air (L^2/T)
- δ_l = thickness of a hypothetical liquid film adjacent to the interface and through which chemical transport is solely by molecular diffusion (L)
- δ_g = thickness of a hypothetical gas film adjacent to the interface and through which chemical transport is solely by molecular diffusion (L)

- r_l = rate of surface renewal for the liquid side of the interface (1/T)
 r_g = rate of surface renewal for the gas side of the interface (1/T).

Film-penetration theory reduces to two-film theory as r_l and r_g become small, and to penetration theory as r_l and r_g become large.

Although values of hypothetical film thicknesses or surface renewal rates are not readily measurable, Equations 2-6 through 2-11 are fundamental for relating mass transfer coefficients between chemicals. Because the influences of hydrodynamic characteristics (δ or r) are independent of chemical concentrations or characteristics in dilute aqueous solutions, the ratio of liquid-phase mass transfer coefficients for two compounds can be expressed as:

$$\Psi_l = \frac{k_{li}}{k_{lj}} = \frac{k_{li}A}{k_{lj}A} = \left\{ \frac{D_{li}}{D_{lj}} \right\}^{n_l} \quad (2-12)$$

where

- Ψ_l = liquid-phase mass transfer relational parameter (-)
 k_{li} = liquid-phase mass transfer coefficient for chemical i (L/T)
 k_{lj} = liquid-phase mass transfer coefficient for chemical j (L/T)
 A = interfacial surface area between water and adjacent air (L²)
 D_{li} = liquid-phase diffusion coefficient for chemical i (L²/T)
 D_{lj} = liquid-phase diffusion coefficient for chemical j (L²/T)
 n_l = liquid-phase power constant (-).

The power constant n_l varies from 0.5 (penetration and surface renewal theory) to 1.0 (two-film theory). Values of n_l have been calculated for natural and engineered systems and are often reported to be between 0.6 and 0.7 (Roberts et al., 1984; Smith et al., 1980). A value of 2/3 is commonly applied. Given a specific value of n_l , Equation 2.12 can be used to estimate k_{li} , given a measured or estimated k_{lj} and the ratio of liquid-phase diffusion coefficients between i and j. The latter are generally available for many volatile chemicals and may also be estimated with a reasonable degree of accuracy (Tucker and Nelken, 1990). Although D_{li} and D_{lj} are both functions of temperature, researchers have observed that Ψ_l does not vary significantly with variations in water temperature, occurrence of surfactants, or degree of turbulent mixing, although the latter may cause variations in n_l (decreasing with an increase in the amount of turbulent kinetic energy in the water) (Matter-Müller et al., 1981; Smith et al., 1980).

In a manner similar to that for k_{li} and k_{lj} , the ratio of gas-phase mass transfer coefficients for two compounds can be expressed as:

$$\Psi_g = \frac{k_{gi}}{k_{gj}} = \left(\frac{D_{gi}}{D_{gj}} \right)^{n_2} \quad (2-13)$$

where

- Ψ_g = gas-phase mass transfer relational parameter (-)
- k_{gi} = gas-phase mass transfer coefficient for chemical i (L/T)
- k_{gj} = gas-phase mass transfer coefficient for chemical j (L/T)
- D_{gi} = gas-phase diffusion coefficient for chemical i (L^2/T)
- D_{gj} = gas-phase diffusion coefficient for chemical j (L^2/T)
- n_2 = power constant (-).

As with the power constant n_1 , n_2 varies between 0.5 and 1.0. Relative to studies involving estimates of n_1 , less work has been reported to confirm appropriate values of n_2 . A value of n_2 equal to 2/3 is often assumed (Little, 1992).

In accordance with Equation 2-4, the ratio of overall mass transfer coefficients for chemicals i and j can be expressed as:

$$\Psi_m = \frac{K_{Li}}{K_{Lj}} = \frac{\frac{1}{k_{lj}} + \frac{1}{k_{gj} \cdot H_{cj}}}{\frac{1}{k_{li}} + \frac{1}{k_{gi} \cdot H_{ci}}} = \frac{\frac{1}{k_{lj}A} + \frac{1}{k_{gj}A \cdot H_{cj}}}{\frac{1}{k_{li}A} + \frac{1}{k_{gi}A \cdot H_{ci}}} \quad (2-14)$$

where

- K_{Li} = overall mass transfer coefficient for chemical i (L/T)
- K_{Lj} = overall mass transfer coefficient for chemical j (L/T)
- A = interfacial surface area between water and adjacent air (L^2)
- k_{li} = liquid-phase mass transfer coefficient for chemical i (L/T)
- k_{lj} = liquid-phase mass transfer coefficient for chemical j (L/T)
- k_{gi} = gas-phase mass transfer coefficient for chemical i (L/T)
- k_{gj} = gas-phase mass transfer coefficient for chemical j (L/T)
- H_{ci} = Henry's law constant for chemical i (L^3_{liq}/L^3_{gas})
- H_{cj} = Henry's law constant for chemical j (L^3_{liq}/L^3_{gas}).

Assuming k_{gi}/k_{ji} is equal to k_{gi}/k_{ji} , Equation 2-14 can be rearranged algebraically to yield:

$$\Psi_m = \frac{K_{Li}}{K_{Lj}} = \Psi_l \Psi_g \frac{\left(\frac{H_{ci}}{H_{cj}} \right) \left[1 + \frac{k_{gj}}{k_{lj}} \frac{H_{cj}}{H_{ci}} \right]}{\left[\Psi_l + \Psi_g \frac{H_{ci}}{H_{cj}} \frac{k_{gj}}{k_{lj}} \right]} \quad (2-15)$$

where

- Ψ_m = overall mass transfer coefficient relational parameter (-)
- K_{Li} = overall mass transfer coefficient for chemical i (L/T)
- K_{Lj} = overall mass transfer coefficient for chemical j (L/T)

$$\Psi_l = \text{liquid-phase mass transfer relational parameter } (-) = \left(\frac{D_{li}}{D_{lj}} \right)^{n_1}$$

- D_{li} = liquid-phase diffusion coefficient for chemical i (L^2/T)
- D_{lj} = liquid-phase diffusion coefficient for chemical j (L^2/T)
- n_1 = liquid-phase power constant (-)

$$\Psi_g = \text{gas-phase mass transfer relational parameter } (-) = \left(\frac{D_{gi}}{D_{gj}} \right)^{n_2}$$

- D_{gi} = gas-phase diffusion coefficient for chemical i (L^2/T)
- D_{gj} = gas-phase diffusion coefficient for chemical j (L^2/T)
- n_2 = power constant (-)
- H_{ci} = Henry's law constant for chemical i (L^3_{liq}/L^3_{gas})
- H_{cj} = Henry's law constant for chemical j (L^3_{liq}/L^3_{gas})
- k_{lj} = liquid-phase mass transfer coefficient for chemical j (L/T)
- k_{gj} = gas-phase mass transfer coefficient for chemical j (L/T).

A common mistake when relating overall mass transfer coefficients between two chemicals is to assume that $K_{Li}/K_{Lj} = \Psi_l$. This relationship requires knowledge only of liquid molecular diffusion coefficients for each compound in accordance with Equation 2-12, but is valid only when gas-phase resistance to mass transfer is negligible for each compound. In fact, Equation 2-

15 converges to Equation 2-12 as k_g/k_l and/or H_c for both i and j become very large. As discussed previously, an assumption that gas-phase resistance is negligible is reasonable when both compounds are highly volatile (e.g., radon). However, for less volatile compounds, it may be necessary to know or estimate not only liquid-phase molecular diffusion coefficients, but also gas-phase molecular diffusion coefficients, Henry's law constants for each chemical, and the ratio of gas-to-liquid phase mass transfer coefficients for the relational surrogate j . Diffusion coefficients and Henry's law constants can be readily obtained or estimated for most chemicals. However, there has not been a significant amount of published information related to k_g/k_l for indoor sources, including its variability with source operating conditions (e.g., liquid flowrate). Thus, an objective of this project was to determine values of k_gA , k_lA , and k_g/k_l for a wide range of operating conditions associated with each experimental system.

2.2. IDEAL REACTOR MODELS

Three ideal reactor models are often used to simulate aqueous and gaseous systems. First, a system may behave as an ideal plug flow reactor (PFR) in which fluid parcels move in an orderly manner without any contact of other fluid parcels in the axial direction, that is, no axial dispersion. A second ideal reactor is a continuous-flow stirred-tank reactor (CFSTR), where fluid parcels are completely mixed within the system such that the concentration within the reactor is the same at all locations. The influent stream of a CFSTR is instantaneously mixed with fluid in the reactor, and the exit stream has the same concentration as fluid within the reactor. Finally, an ideal batch reactor may be used to describe systems where fluid is initially introduced to a system as a well-mixed uniform solution, after which no fluid enters or leaves the reactor. Most household water systems have behavior that falls between these ideal cases. However, instead of developing nonideal flow models, for this project each experimental system was analyzed as though it were ideal. Deviations from the assumed ideal case are reflected in the experimentally determined mass transfer coefficients.

2.2.1. Plug Flow Reactor Model

A schematic of a plug flow reactor is shown in Figure 2-1. The associated mass balance equation for a differential element of volume ΔV is:

$$\frac{d(CV)}{dt} = (QC)|_z - (QC)|_{z+\Delta z} + \sum_{r_v} \Delta V + \sum_{r_A} \Delta A \quad (2-16)$$

where

C = chemical concentration (M/L^3)

V	=	volume (L^3)
t	=	time (T)
ΔA	=	differential area (L^2)
Q	=	volumetric flowrate (L^3/T)
r_V	=	volume reaction rate ($M/L^3 \cdot T$)
ΔV	=	differential volume (L^3)
r_A	=	area reaction rate ($M/L^2 \cdot T$)
z	=	direction of flow.

2.2.2. Continuous-Flow Stirred-Tank Reactor Model

The following equation applies to the CFSTR depicted in Figure 2-2:

$$\frac{d(CV)}{dt} = \sum_{i=1}^n Q_{jn,j} C_{jn,j} - Q_{out,total} C + a^p r_{V,j} V + a^q r_{A,j} A_j \quad (2-17)$$

where

C	=	chemical concentration in reactor (M/L^3)
V	=	volume (L^3)
Q_{in}	=	inlet volumetric flowrate (L^3/T)
C_{in}	=	inlet chemical concentration (M/L^3)
Q_{out}	=	outlet volumetric flowrate (L^3/T)
r_V	=	volume reaction rate ($M/L^3 \cdot T$)
r_A	=	area reaction rate ($M/L^2 \cdot T$)
A	=	area (L^2).

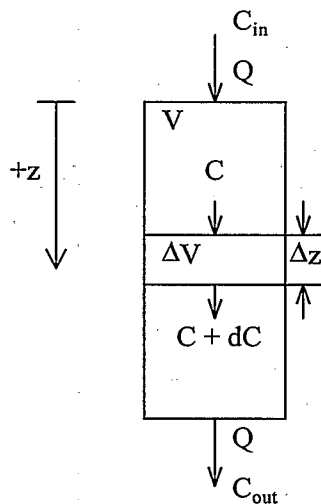


Figure 2-1. Plug flow reactor.

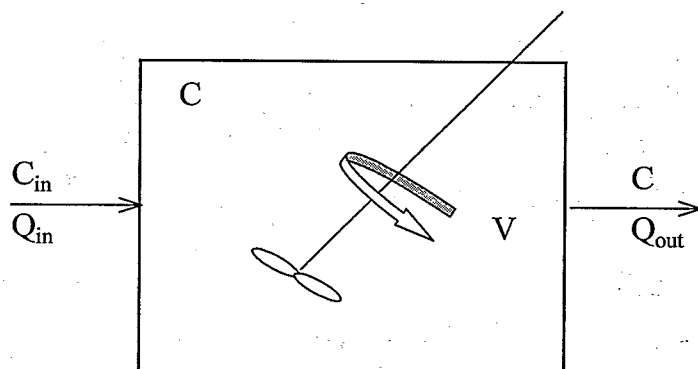


Figure 2-2. Continuous-flow stirred-tank reactor.

2.2.3. Batch Reactor Model

A batch reactor is merely a simplified CFSTR, that is, a well-mixed solution with no volumetric flowrate terms. A mass balance on the batch reactor shown in Figure 2-3 is:

$$\frac{d(CV)}{dt} = \overset{\circ p}{a} r_{v,j} V + \overset{\circ q}{a} r_{A,j} A_j \quad (2-18)$$

where

- C = chemical concentration in reactor (M/L³)
- V = volume (L³)
- r_v = volume reaction rate (M/L³•T)
- r_A = area reaction rate (M/L²•T)
- A = area (L²).

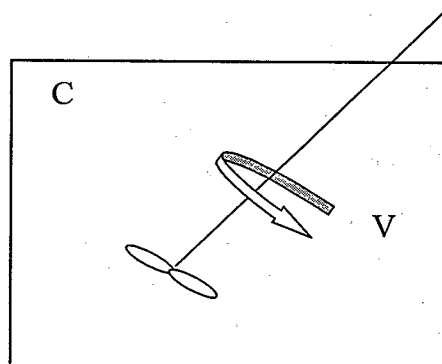


Figure 2-3. Batch reactor.

2.3. SOURCE-SPECIFIC MASS BALANCE MODELS

Development of source-specific mass balance models involved the following steps: (1) defining the system's phase boundaries and (2) determining which ideal flow model most accurately represented each phase. The mass balances for each source, as well as solutions to the resulting differential equations, are given in this section.

2.3.1. Dishwasher Models

Dishwasher operation consists of pumping hot water through a rotating spray arm that produces liquid droplets that impact surrounding surfaces. The volume of liquid used in operation is recycled, that is, the liquid volume is constant. Typical dishwasher operation consists of four cycles: prerinse, wash, rinse, and final rinse. Within each cycle is a fill period, the cycling of water, and a drain period. The fill and drain periods are significantly shorter (100 seconds each) than the cycling of water, and were not modeled for this study.

Figure 2-4 represents a dishwasher, for which the liquid phase is treated as a well-mixed batch reactor. Chemical volatilization is primarily due to the formation and spraying of droplets. Following Equation 2-18 with the only reaction term being the transfer of mass across the water/air interface (see Equation 2-3), a mass balance on the liquid phase leads to:

$$\frac{d(C_1 V_1)}{dt} = -K_L C_1 - \frac{C_g}{H_c} A \quad (2-19)$$

where

- C_1 = chemical concentration in water (M/L³)
- V_1 = volume of water (L³)
- t = time (T)
- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- C_g = chemical concentration in air adjacent to water (M/L³)
- H_c = Henry's law constant for chemical of interest (L³_{liq}/L³_{gas})
- A = interfacial surface area between water and adjacent air (L²).

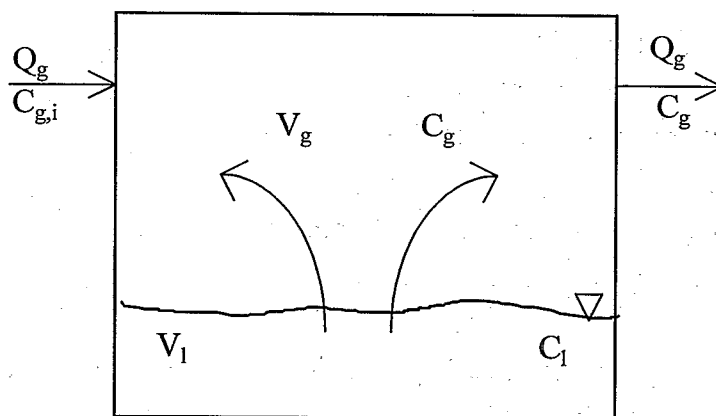


Figure 2-4. Dishwasher model.

Assuming the liquid volume is constant during operation, the liquid-phase mass balance may be rewritten as:

$$\frac{dC_l}{dt} = -\frac{K_L A}{V_l} C_l + \frac{K_L A}{V_l H_c} C_g \quad (2-20)$$

where

- C_l = chemical concentration in water (M/L^3)
- V_l = volume of water (L^3)
- t = time (T)
- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- C_g = chemical concentration in air adjacent to water (M/L^3)
- H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas})
- A = interfacial surface area between water and adjacent air (L^2).

The dishwasher headspace (gas phase) is assumed to approach a CFSTR, also with a single reaction term related to mass transfer across the water/air interface. A corresponding mass balance leads to:

$$\frac{d(C_g V_g)}{dt} = Q_g C_{g,in} - Q_g C_g + K_L C_l - \frac{C_g}{H_c} A \quad (2-21)$$

where

- C_g = chemical concentration in air adjacent to water (M/L^3)
- V_g = headspace volume (L^3)

- t = time (T)
 Q_g = ventilation rate (L^3/T)
 $C_{g,in}$ = gas concentration entering system from outside air (M/L^3)
 K_L = overall mass transfer coefficient for the chemical of interest (L/T)
 C_l = chemical concentration in water (M/L^3)
 H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas})
 A = interfacial surface area between water and adjacent air (L^2).

Assuming the gas volume is constant during operation and the background air is relatively clean ($C_{g,in} = 0$), Equation 2-21 may be rewritten as:

$$\frac{dC_g}{dt} = \frac{K_L A}{V_g} C_l - \frac{Q_g}{V_g} + \frac{K_L A}{V_g H_c} C_g \quad (2-22)$$

where

- C_g = chemical concentration in air adjacent to water (M/L^3)
 V_g = headspace volume (L^3)
 t = time (T)
 Q_g = ventilation rate (L^3/T)
 K_L = overall mass transfer coefficient for the chemical of interest (L/T)
 C_l = chemical concentration in water (M/L^3)
 H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas})
 A = interfacial surface area between water and adjacent air (L^2).

Equations 2-20 and 2-22 must be solved simultaneously in order to determine $K_L A$.

$$\left(\frac{BF}{Z} + \frac{EC_{l,0}}{Z} - \frac{DC_{l,0}}{2} \right) \left[\frac{1}{\sqrt{\frac{D^2}{4} - E}} \exp\left(-\frac{D}{2}t\right) \sinh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) \right]$$

Analysis using Laplace transforms leads to:

$$C_l = C_{l,0} \left[\exp\left(-\frac{D}{2}t\right) \cosh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) \right] + \quad (2-23)$$

and

$$C_g = C_{g,0} \exp\left(-\frac{D}{2}t\right) \cosh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) + \left(F - \frac{DC_{g,0}}{2}\right) \left[\frac{1}{\sqrt{\frac{D^2}{4} - E}} \exp\left(-\frac{D}{2}t\right) \sinh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) \right] \quad (2-24)$$

where

$C_{l,0}$ = initial liquid concentration (M/L³)

$C_{g,0}$ = initial gas concentration (M/L³)

$$Z = \frac{K_L A}{V_l}$$

K_L = overall mass transfer coefficient for the chemical of interest (L/T)

A = interfacial surface area between water and adjacent air (L²)

V_l = volume of water (L³)

$$B = \frac{K_L A}{V_l H_c}$$

H_c = Henry's law constant for chemical of interest (L³_{liq}/L³_{gas})

$$X = \frac{K_L A}{V_g}$$

V_g = headspace volume (L³)

$$Y = \frac{Q_g}{V_g} + \frac{K_L A}{V_g H_c}$$

Q_g = ventilation rate (L³/T)

$D = Z + Y$

$E = ZY - BX$

$F = ZC_{g,0} + XC_{l,0}$

The method used to determine $K_L A$ based on experimental data is presented in Section 3.6.

2.3.2. Washing Machine Models

Typical operation of a residential washing machine consists of the following sequence of events: fill, wash, spin, fill, rinse, and spin. The fill cycle consists of a falling film that impacts an underlying pool that continuously increases in depth. Chemical volatilization may be attributed to the falling film, splashing at the surface, and entrained air bubbles. The wash and rinse cycles both involve agitation of the basin water for a specific length of time. The only differences between the wash and rinse cycles are the presence of detergent for the wash cycle and the time of agitation. The primary mass transfer mechanism associated with these cycles is volatilization across the agitated water/air interface. Finally, during a spin cycle the washing machine basket is rotated at a rapid rate such that the respective wash and rinse water is removed from the clothing and pumped from the machine. It was assumed that minimal chemical volatilization occurs during a spin cycle because of lower water volume and shorter contact time between the contaminated water and headspace air. The rate of chemical volatilization from a washing machine was characterized through independent investigations of the fill and wash/rinse cycles.

2.3.2.1. Washing Machine Fill Cycle

A washing machine fill cycle is represented in Figure 2-5. Water enters a machine with a constant inlet concentration and accumulates in the washing machine basin. On the basis of visual observation of turbulence in the underlying pool and a short residence time for the falling film, volatilization from the latter was assumed to be insignificant. A mass balance on the liquid phase is based on a CFSTR such that:

$$\frac{d(C_1 V_1)}{dt} = Q_1 C_{1,in} - K_L C_1 - \frac{C_g}{H_c} A \quad (2-25)$$

where

- C_1 = chemical concentration in water (M/L^3)
- V_1 = volume of water (L^3)
- t = time (T)
- Q_1 = liquid fill rate (L^3/T)
- $C_{1,in}$ = inlet liquid-phase concentration (M/L^3)
- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- C_g = chemical concentration in air adjacent to water (M/L^3)
- H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas})
- A = interfacial surface area between water and adjacent air (L^2).

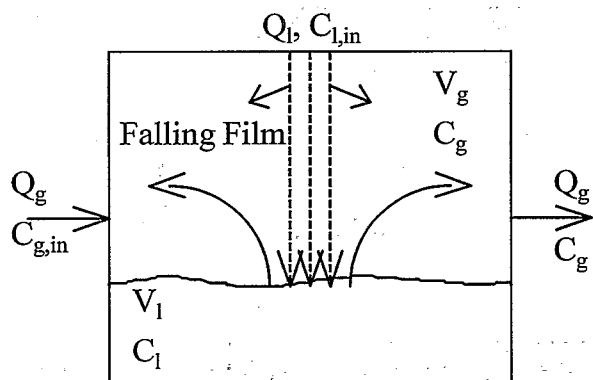


Figure 2-5. Washing machine fill cycle model.

The gas phase of the system is also assumed to approach a continuous-flow stirred-tank reactor. A corresponding mass balance leads to:

$$\frac{d(C_g V_g)}{dt} = Q_g C_{g,in} - Q_g C_g + K_L \left(C_l - \frac{C_g}{H_c} \right) A \quad (2-26)$$

where

- C_g = chemical concentration in air adjacent to water (M/L^3)
- V_g = headspace volume (L^3)
- t = time (T)
- Q_g = ventilation rate (L^3/T)
- $C_{g,in}$ = gas concentration entering system from outside air (M/L^3)
- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- C_l = chemical concentration in water (M/L^3)
- H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas})
- A = interfacial surface area between water and adjacent air (L^2).

As with the gas-phase mass balance for dishwashers, Equation 2-26 may be simplified by assuming that the background air is relatively clean. However, unlike the dishwasher gas-phase mass balance, the washing machine gas-phase volume is changing with time as the liquid fills the machine and must therefore remain as part of the derivative.

In order to determine $K_L A$ during filling, Equations 2-25 and 2-26 were solved simultaneously. However, since the liquid and gas-phase volumes and chemical concentrations

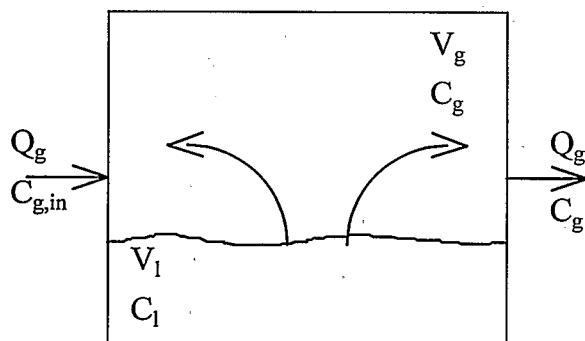


Figure 2-6. Washing machine wash/rinse cycle model.

are changing with time, a numerical solution technique was adopted to determine $K_L A$. This method is presented in Section 3.6.

2.3.2.2. Washing Machine Wash/Rinse Cycles

The liquid phase for a wash/rinse cycle was treated as a well-mixed batch reactor with a constant liquid volume (Figure 2-6). The liquid- and gas-phase mass balances for this system are identical to the liquid- and gas-phase mass balances for a dishwasher (Equations 2-20 and 2-22). Thus, the solutions given in Equations 2-23 and 2-24 also apply for this source.

2.3.3. Shower Models

Mass balance equations for a shower (as shown in Figure 2-7) were developed previously by Little (1992). A summary of these equations, and their derivation, is provided in the text below.

Little (1992) identified the regions within a shower system where mass transfer occurs: drop formation, drop acceleration to terminal velocity, fall of drop at terminal velocity, and impact of drop on shower stall surfaces. To predict the rate of mass transfer from liquid droplets to the surrounding air, Little modeled the liquid phase as a plug-flow system with the following mass balance:

$$\frac{dC_l}{dz} = - \frac{K_L \left(C_l - \frac{C_g}{H_c} \right) P}{Q_l} \quad (2-27)$$

where

C_l = chemical concentration in water (M/L^3)

K_L = overall mass transfer coefficient for the chemical of interest (L/T)

- C_g = chemical concentration in air adjacent to water (M/L^3)
 H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas})
 Q_l = liquid flowrate (L^3/T)
 z = direction of flow
 P = perimeter of water stream (L).

The residence time of a water droplet was assumed to be relatively short. This assumption allowed the gas-phase concentration in Equation 2-27 to be considered constant. The resulting differential equation was solved to give:

$$C_{l,out} = C_{l,in} \exp\left(-\frac{K_L A}{Q_l}\right) + \left(\frac{C_g}{H_c}\right) \left(1 - \exp\left(-\frac{K_L A}{Q_l}\right)\right) \quad (2-28)$$

where

- $C_{l,out}$ = outlet chemical concentration in water (M/L^3)
 $C_{l,in}$ = inlet chemical concentration in water (M/L^3)
 K_L = overall mass transfer coefficient for the chemical of interest (L/T)
 PL = interfacial area (L^2)
 P = perimeter of water stream (L)
 L = length of stream of water (L)

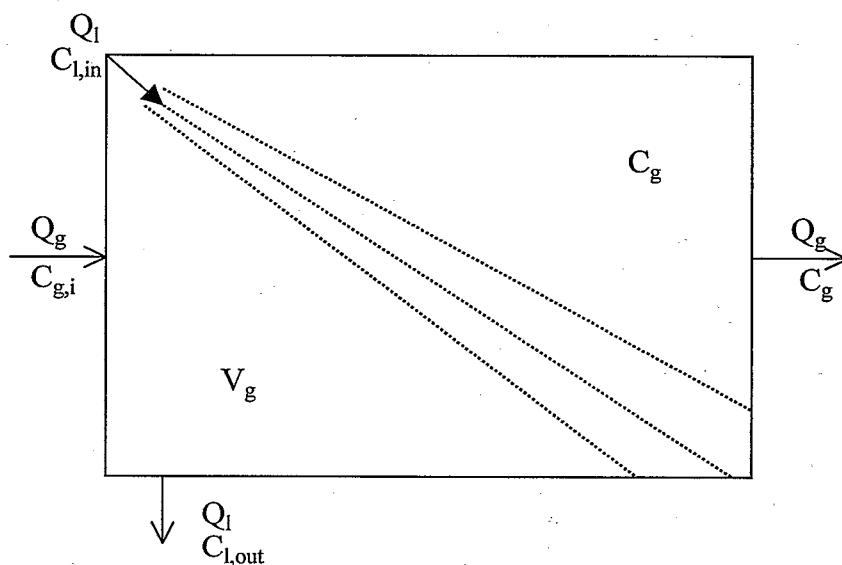


Figure 2-7. Shower model.

Q_l	=	liquid flowrate (L^3/T)
C_g	=	chemical concentration in air adjacent to water (M/L^3)
H_c	=	Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas}).

Little (1992) also developed a mass balance to characterize the change in gas-phase concentration during shower operation. He modeled the gas phase as a CFSTR with the transfer of mass from the liquid being the difference between the mass flowrate of chemical entering the system and the mass flowrate of chemical leaving the system ($Q_l C_{l,in} - Q_l C_{l,out}$). The following equation was applied:

$$V_g \frac{dC_g}{dt} = Q_l(C_{l,\epsilon} - C_{l,out}) - Q_g(C_g - C_{g,\epsilon}) \quad (2-29)$$

where

C_g	=	chemical concentration in air adjacent to water (M/L^3)
V_g	=	shower stall volume (L^3)
t	=	time (T)
Q_l	=	liquid flowrate (L^3/T)
$C_{l,in}$	=	inlet chemical concentration in water (M/L^3)
$C_{l,out}$	=	outlet chemical concentration in water (M/L^3)
Q_g	=	ventilation rate (L^3/T)
$C_{g,in}$	=	inlet chemical concentration in air (M/L^3).

The solution to the gas-phase mass balance was achieved by substituting Equation 2-28 into Equation 2-29 and then integrating, to yield:

$$C_g = \frac{B}{D} + \left(C_{g,0} - \frac{B}{D} \right) \exp(-Dt) \quad (2-30)$$

where

$C_{g,0}$	=	initial gas concentration (M/L^3)
t	=	time (T)

$$B = \frac{\left(Q_l C_{l,\epsilon} \left(1 - \exp\left(-\frac{K_L A}{Q_l} \right) \right) + Q_g C_{g,\epsilon} \right)}{V_g} \quad (M/L^3 \cdot T)$$

Q_l = liquid flowrate (L^3/T)

$C_{l,in}$ = inlet chemical concentration in water (M/L^3)

K_L = overall mass transfer coefficient for the chemical of interest (L/T)

A = interfacial area (L^2)

Q_g = ventilation rate (L^3/T)

$C_{g,in}$ = inlet chemical concentration in air (M/L^3)

V_g = shower stall volume (L^3)

$$D = \frac{\left(\left(\frac{Q_l}{H_c} \right) \left(1 - \exp \left(- \frac{K_L A}{Q_l} \right) \right) + Q_g \right)}{V_g} \quad (1/T)$$

H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas}).

Values of $K_L A$ may be estimated using Equations 2-28 and 2-30. The corresponding solution technique is presented in Section 3.6.

2.3.4. Bathtub Models

Three distinct operations are associated with a bathtub: (1) water flowing through the faucet with the drain open (flow-through), (2) filling the tub, and (3) bathing in a filled tub. Each operation has a different associated mass balance model.

2.3.4.1. Bathtub Flow-Through Model

When water is flowing through the faucet with the drain open, there is no accumulation of water in the basin. This type of operation is depicted in Figure 2-8 and may be treated in a manner similar to that of a shower, such that Equations 2-27 and 2-29 apply.

2.3.4.2. Bathtub Fill Model

The filling of a bathtub (Figure 2-9) is similar to the washing machine fill cycle, whose mass balance equations were given in Section 2.3.2.1. The numerical solution technique adopted for a bathtub is provided in Section 3.6.

2.3.4.3. Bathtub Surface Volatilization Model

Finally, once the tub is filled, chemical mass transfer may continue across the water/air interface. As shown in Figure 2-10, there are no more inputs or outputs of mass, such that the

system may be modeled in a manner similar to that of a dishwasher (see Section 2.3.1) and washing machine wash/rinse cycles (see Section 2.3.2.2).

2.4. CHEMICAL EMISSION MODELS

A valuable product of this work is the ability to predict human inhalation exposure to contaminants present in drinking water. The level of human exposure is directly related to the gas-phase chemical concentration, which may be estimated using the appropriate source-specific mass balance models presented in Section 2.3. In addition to C_g , system and environmental conditions are also important for predicting human exposure, for example, room volume, air exchange rate, or headspace ventilation rate.

For dishwashers and washing machines, humans are exposed to chemicals emitted from the headspace within each respective machine. This emission rate is equivalent to:

$$E_{\text{chem}} = Q_g C_{g,t} \quad (2-31)$$

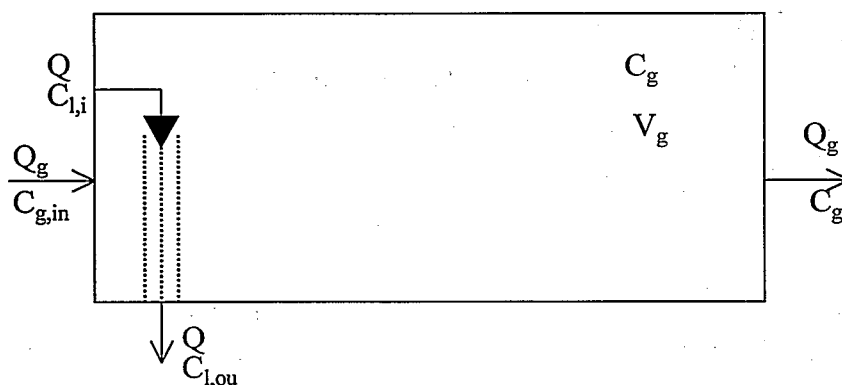


Figure 2-8. Bathtub flow-through model.

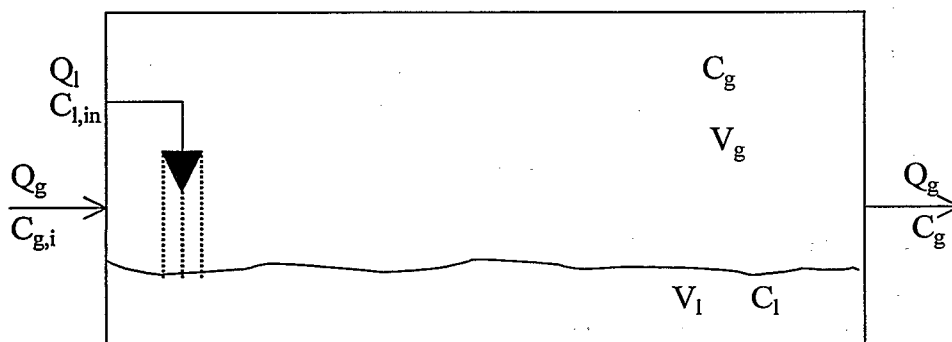


Figure 2-9. Bathtub fill model.

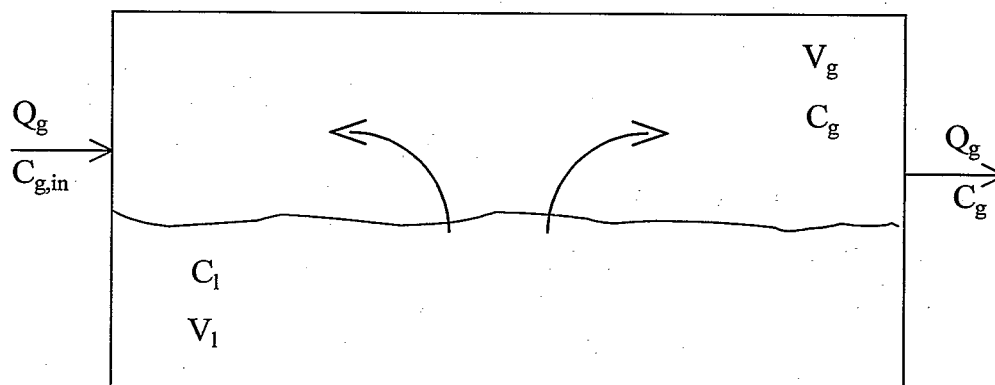


Figure 2-10. Bathtub surface volatilization model.

where

- E_{chem} = chemical mass emission rate (M/T)
- Q_g = machine headspace ventilation rate (L^3/T)
- $C_{g,t}$ = time-dependent gas-phase chemical concentration in machine headspace (M/L^3).

Equation 2-31 may be used to estimate a chemical mass emission rate profile for the duration of machine operation. Integration under this curve results in total chemical mass emitted during the event. Resulting human exposure may be predicted by incorporating the mass emission rate profile into a mass balance on the associated room air. An application of these models is presented in Chapter 8.

In showers and bathtubs, humans receive a more "direct" exposure to volatilized chemicals. Assuming no other losses, the mass flowrate for a plug-flow system is equivalent to:

$$E_{\text{chem}} = Q_l (C_{l,\text{in}} - C_{l,\text{out}}) \quad (2-32)$$

where

- E_{chem} = chemical mass emission rate (M/T)
- Q_l = liquid flowrate (L^3/T)
- $C_{l,\text{in}}$ = liquid-phase concentration entering system (M/L^3)
- $C_{l,\text{out}}$ = liquid-phase concentration leaving system (M/L^3).

Mass emissions during a bathing event may be determined using:

$$E_{chem} = K_L A \left(C_l - \frac{C_g}{H_c} \right) \quad (2-33)$$

where

- E_{chem} = chemical mass emission rate (M/T)
- K_L = overall mass transfer coefficient for the chemical of interest (L/T)
- A = interfacial area (L^2)
- C_l = chemical concentration in water (M/L^3)
- C_g = chemical concentration in air adjacent to water (M/L^3)
- H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas}).

As with dishwashers and washing machines, the mass emission rate profile may be developed for the duration of a showering or bathing event. Example applications of mass emission models are presented in Chapter 8.

3. GENERAL METHODOLOGY

There is currently no standardized protocol for measuring volatilization rates from indoor sources. Thus, a general protocol was developed for this project and was applied to all sources. Common features of this protocol follow:

1. A stainless steel source chamber
2. Chemical tracers
3. Chemical sampling
4. Sample analysis
5. Quality assurance measures
6. Data analysis
7. Mass closure assessments

The experimental methodology and associated quality assurance measures applicable to all sources are presented in this section. Methodologies specific to individual sources are discussed in the respective source chapters (Chapters 4 to 7).

3.1. SOURCE CHAMBER

Previous experimental studies vary in their isolation of household tap water sources of volatilization, which range from abandoned houses to laboratories and exposure chambers. All experiments for this project were completed within a stainless steel exposure chamber. The chamber was $2.4 \text{ m} \times 1.8 \text{ m} \times 2.4 \text{ m}$ (11 m^3 in volume). It was ventilated under negative pressure; that is, air was drawn into the chamber and exhausted through a ceiling port connected to a fume hood. The enclosed chamber had the advantages of allowing for a mass closure assessment through the measurement of both liquid- and gas-phase concentrations and volumetric flowrates. Although washing machines and dishwashers effectively served as their own exposure chambers, the experiments involving these sources were also completed in the stainless steel chamber.

3.2. CHEMICAL TRACERS

3.2.1. Physicochemical Properties

All experiments were completed using a chemical cocktail containing five volatile tracers: acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane. These five chemicals represent a wide range of Henry's law constants. Physicochemical properties for each chemical are given in Table 3-1. The five chemicals were chosen to meet the following requirements:

8. At least one chemical had an $H_c > 1.0 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ at 25°C.
9. At least one chemical had an $H_c < 0.005 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ at 25°C.
10. Two chemicals had similar physicochemical properties, that is, similar H_c and molecular diffusion coefficients.
11. All chemicals had the capability of being analyzed with the same gas chromatography (GC) system and flame ionization detector (FID), with adequate separation of peaks.
12. Chemicals were easily identified and quantified by GC/FID at low aqueous-phase concentrations ($< 500 \mu\text{g/L}$) to minimize chemical usage and discharge during experiments.
13. Chemicals had a solubility $> 10 \text{ mg/L}$ in water.
14. At desired concentrations, chemicals posed minimum risks to researchers during experiments.

Henry's law constants for chemicals used in experiments completed at temperatures other than 25°C were adjusted to reflect the temperature change. To determine the change in Henry's law constant with increasing or decreasing temperature, existing equations developed by Ashworth et al. (1988) were used for toluene, ethylbenzene, and cyclohexane.

Table 3-1. Summary of physicochemical properties for selected chemical tracers

Compound	H_c @ 25°C ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$)	D_l @ 24°C (cm^2/s)	D_g @ 24°C (cm^2/s)	T_b (°C)	ρ (kg/L)	Solubility (mg/L)	P_v° (mm Hg)
Acetone	0.0015	1.1E-05	0.11	56.5	0.79	miscible	270
Ethyl Acetate	0.0050	9.5E-06	0.092	77.0	0.89	64000	115
Toluene	0.27	9.1E-06	0.085	110.6	0.87	515	22.0
Ethylbenzene	0.33	8.4E-06	0.077	136.2	0.87	152	7.0
Cyclohexane	7.2	9.0E-06	0.088	80.7	0.77	58	77

Sources: Ashworth (1988), CRC Handbook (1995), Howard (1990) and Tucker and Nelken (1990).

These equations have been validated for a temperature range of 10°C to 30°C.

$$\text{Toluene: } H_{c,T} = \exp[5.133 - 3024/(T + 273.15)] / (0.000082 * (T + 273.15)) \quad (3.1)$$

$$\text{Ethylbenzene: } H_{c,T} = \exp[11.92 - 4994/(T + 273.15)] / (0.000082 * (T + 273.15)) \quad (3.2)$$

$$\text{Cyclohexane: } H_{c,T} = \exp[9.141 - 3238/(T + 273.15)] / (0.000082 * (T + 273.15)) \quad (3.3)$$

where

$H_{c,T}$ = Henry's law constant at experimental temperature (L^3_{liq}/L^3_{gas})

T = experimental temperature (°C).

Schoene and Steinhanses (1985) developed the following relationship between Henry's law constant and temperature for acetone.

$$\text{Acetone: } \log(H_{c,T}) = -2218/(T + 273.15) + 4.545 \quad (3.4)$$

where

$H_{c,T}$ = Henry's law constant at experimental temperature (L^3_{liq}/L^3_{gas})

T = experimental temperature (°C).

There is a lack of published information related to temperature effects on Henry's law constant for ethyl acetate. The following relationship was used to predict the change in ethyl acetate's Henry's law constant at different experimental temperatures (Enviromega, 1993).

$$\text{Ethyl Acetate: } H_{c,T} = H_{c,25^\circ\text{C}} \cdot 1.044^{(T-25^\circ\text{C})} \quad (3.5)$$

where

$H_{c,T}$ = Henry's law constant at experimental temperature (L^3_{liq}/L^3_{gas})

$H_{c,25^\circ\text{C}}$ = Henry's law constant at 25°C (L^3_{liq}/L^3_{gas})

T = Experimental temperature (°C).

3.2.2. Chemical Tracer Addition

The water used in each experimental system was spiked with a multitracer stock solution. Tracer solutions were prepared in 3 L Tedlar™ bags fitted with a stainless steel hose/valve with

locking screw and a replaceable Teflon™-lined septum with a stainless steel cap. Tedlar™ bags were ideal for preparing and transferring volatile tracer solutions because of the minimal headspace associated with filling and emptying the bag with liquid. A bag had the capability to expand or collapse without forming a headspace. Each bag was filled with cold tap water using a variable-speed peristaltic pump (Masterflex™ Laboratory Standard Variable Speed Drive System). Teflon™ tubing (0.635 cm OD) dedicated to clean water usage provided the means of water transfer through the inlet valve of each bag. Any air added during this procedure was removed by collecting it in a large bubble near the bag's valve opening and reversing the pump, thereby emptying the excess air. Syringes adequately cleaned with methanol and water were used for chemical injections. Known amounts of each chemical were injected into a known volume of tap water contained in the Tedlar™ bag. In addition to resulting system concentrations, chemical solubilities were considered when determining the volume of chemical to be added. To facilitate dissolution, bags were manually agitated and allowed to sit for periods over 24 hours prior to use in any experiments.

The predissolved solution had to be added to the water supply of each experimental system. To add the chemical solution, the Masterflex™ peristaltic pump described above with Teflon™ tubing dedicated to chemical addition was used. As the bags were emptied, the chemical solution was manually mixed into the system's water supply. Additional experimental procedures are presented in each respective source chapter (Chapters 4 to 7).

3.3. CHEMICAL SAMPLING

3.3.1. Liquid-Phase Sampling

Each experimental system was retrofitted with a liquid sample port made of Teflon™. This port was designed to minimize chemical losses during sampling, for example, preventing air in the sample line. In addition, Teflon™ tubing was connected to the end of the sample port such that when a liquid sample was collected the water entered near the bottom of the sample vial, thereby minimizing splashing. Liquid samples were collected in 22 mL glass vials and sealed with an aluminum cap fitted with a Teflon™-faced silicon septum. Approximately 11 mL of water were collected in each vial, leaving a significant headspace in the vial.

Samples were stored at 4°C in a laboratory refrigerator until analysis. Preexperimental tests determined that samples could be stored up to 1 week at 4°C without significant losses. Samples moved to another location for analysis were transported in an ice chest at a temperature at or below 4°C. A data log book contained a record of each liquid sample including information regarding date of collection, date of transport (if necessary), length of storage, and date of analysis.

3.3.2. Gas-Phase Sampling

Each experimental system was also retrofitted with a stainless steel Swagelok™ gas sample port. Gas samples were collected on Carbotrap™ 300 (Supelco™) adsorbent tubes (0.635 cm OD × 17.8 cm). Carbotrap™ adsorbent tubes were packed with graphitized carbon black and were determined to be suitable for trapping and thermally desorbing the target organic compounds. Samples were collected using a gas sample pump and bubble flowmeter in series as shown in Figure 3-1. The sorbent tube was attached to the Swagelok™ port open to the experimental system's headspace from which gas was drawn. The flowrate at which gas was drawn through the sorbent tube was measured by the bubble flowmeter. The volume of air drawn through the sorbent tube was determined by timing the event. Sample flowrates were in the range of 0.15 to 0.55 L/minute. For batch and flowthrough experiments, sampling times ranged from 30 to 60 seconds and were scheduled such that a liquid sample was collected during the gas sampling period. For fill cycle experiments, a single gas sample was collected for the duration of the 3- to 6-minute experiments. Preliminary tests were completed to ensure that experimental sample tubes were not achieving breakthrough at these sampling conditions.

Once the gas sample had been collected, the ends of the sorbent tube were sealed with stainless steel Swagelok™ caps and stored at 4°C in a hermetically sealed jar containing activated carbon. Again, it was determined through preexperimental testing that gas samples could be stored up to 1 week without sample loss at these conditions.

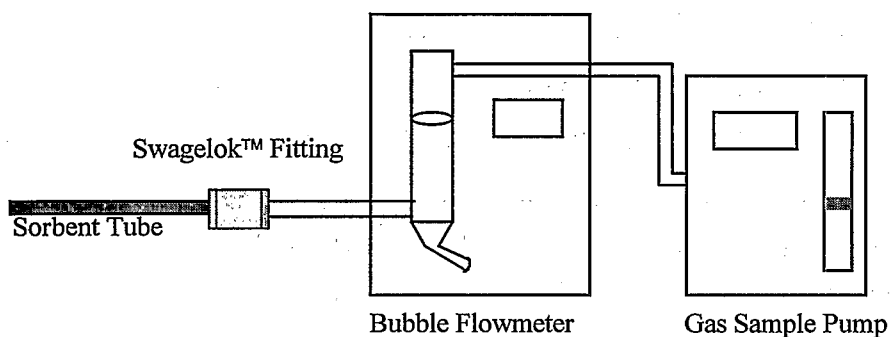


Figure 3-1. Gas sampling experimental setup.

3.4. SAMPLE ANALYSES

3.4.1. Liquid Sample Analysis

Liquid samples were analyzed using a headspace concentrator equipped with an autosampler (Tekmar 7000) and a gas chromatograph (Hewlett Packard, 5890 Series II Plus) with a flame ionization detector (GC/FID). Method parameters for the headspace concentrator were based on previous experimental work and were as follows: sealed vials containing liquid samples were lowered into a platen chamber where they were heated at 70°C for 60 minutes, allowing the volatile organic compounds to be transferred into the vial headspace and to reach equilibrium. Equilibrium concentration is highly dependent on temperature, and a platen temperature of 70°C was determined to be an optimum value for this study. Each liquid sample was heated for identical periods of time and temperatures, thus enhancing reproducibility. Following the platen equilibration time, the vial was pressurized with helium for 1 minute. The sample loop was then filled for 1 minute and allowed to stabilize for 0.2 minutes. To prevent condensation, the sample loop temperature was set at 100°C. The headspace sample was then injected for one minute into the gas chromatograph at a temperature of 100°C.

The GC/FID parameters included an inlet temperature of 200°C and a detector temperature of 250°C, once again preventing condensation. For each sample, the initial oven temperature was 32°C, which was held constant for 0.5 minutes before being ramped at 20°C/minute to a final oven temperature of 55°C. This final temperature was held constant for 1 minute, leading to a total run time of 2.65 minutes. Over the course of the experimental period, different GC/FID columns were

used. Analytical columns included a Restek™ capillary column (30 m × 0.53 mm × 3.0 μm film thickness) and an HP-1 capillary column (5 m × 0.53 mm × 2.65 μm film thickness).

Chromatographic peaks were drawn and integrated using HP 3365 Series II ChemStation (Version A.03.34) software. A sample chromatogram is shown in Figure 3-2, where the abscissa is time and the ordinate is the GC/FID response.

Liquid samples were analyzed within 1 week of collection, typically on the same day of collection. To limit column contamination, the vials were placed on the headspace autosampler tray in the order of increasing concentration. Vials containing clean water (blanks) were placed intermittently between sample vials, and served as indicators of system contamination, which was always minimal.

3.4.2. Liquid Standards

For each experiment, an additional stock solution was prepared as described in Section 3.2.2 for the preparation of liquid standards. Ten milliliters of cold tap water were added to a 22 mL glass vial using a volumetric glass pipette. The vial was sealed with a Teflon™-faced silicon septum and aluminum cap using a hand-held crimper. A small volume of stock solution with a known concentration of each chemical was injected into a solution with a known volume of clean water.

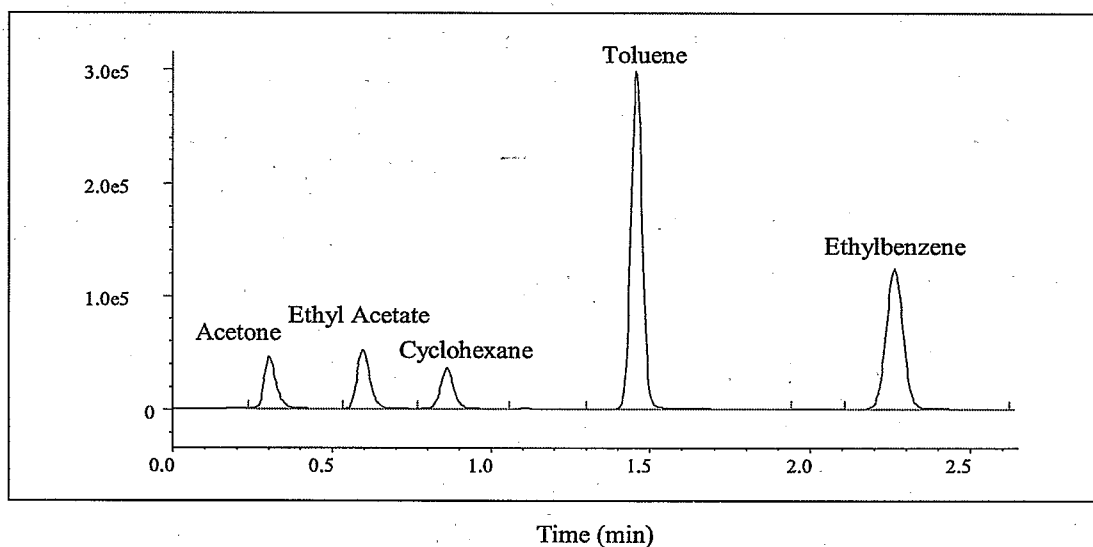


Figure 3-2. Liquid-phase sample chromatogram.

The resulting concentrations of each chemical in the vial were calculated. By varying the amount of stock solution extracted from the bag, six vials with different concentrations were prepared. These standards were used to develop a six-point linear calibration curve, for example, gas chromatograph area response versus chemical concentration. The six calibration points were chosen based on experimental data, such that liquid sample measurements were within the range of standards. A sample liquid calibration curve is shown in Figure 3-3. External calibration curves for each tracer had a coefficient of determination (R^2) of at least 0.95 and were nearly always greater than 0.98.

Since several experiments incorporated the use of detergent, a separate test was completed to determine the effects of detergent on chemical calibration curves. Using a single stock solution, two calibration curves were developed: one using clean (no detergent present) water as the matrix and a second using "soapy" water as the matrix. In a comparison of the two curves, only ethyl acetate was significantly affected by the presence of detergent in the water. This impact is further discussed in appropriate source-specific chapters.

As described in Section 3.2.2, it is conceivable that complete dissolution of some tracers, particularly cyclohexane, did not occur prior to the development of calibration curves. In such cases, liquid-phase concentrations may have been overestimated. This is likely the reason for relatively poor mass closures for cyclohexane during many experiments. However, stripping efficiencies and mass transfer coefficients for cyclohexane should not have been affected by this phenomenon. This

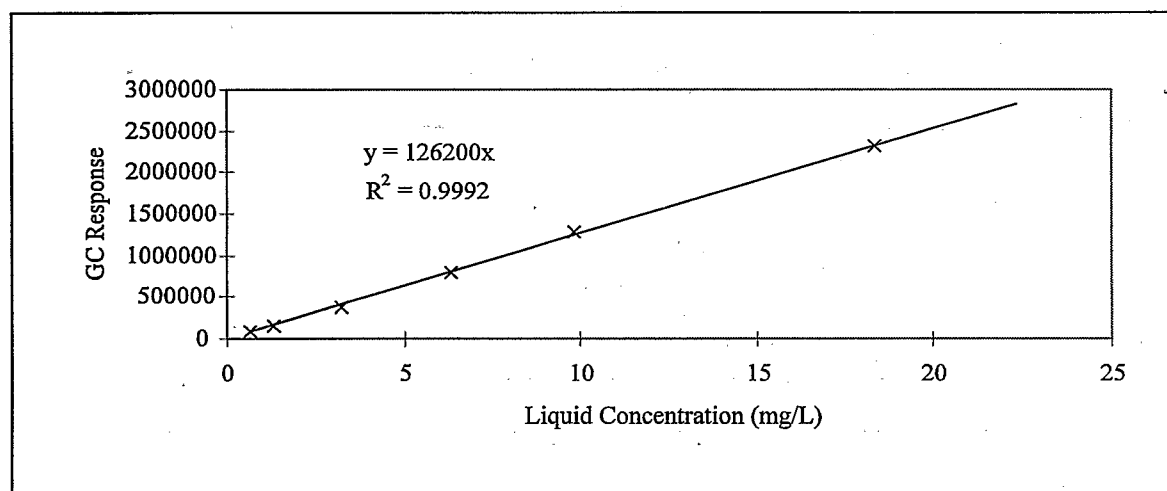


Figure 3-3. Liquid-phase calibration curve for ethylbenzene.

is true because all stripping efficiencies and mass transfer coefficients for cyclohexane were based on relative changes in liquid concentrations.

3.4.3. Gas Sample Analysis

Gas samples were analyzed using a thermal desorber with an autosampler (Tekmar 6016) and a purge and trap concentrator (Tekmar 3000). Over the course of the experimental period, this system was plumbed to different gas chromatographs. First, it was plumbed to the GC/FID described in Section 3.4.1. Most recently, the system was plumbed to a gas chromatograph (Hewlett Packard, 6890 Series) with a flame ionization detector (GC/FID#2). Method parameters for the thermal desorber and purge and trap system were based on recommended values for Carbotrap™ 300 sorbent tubes. Each tube was heated at 200°C for 8 minutes. The desorbed contaminants were transported to the purge and trap column through a transfer line with a temperature of 200°C. Once the desorption phase was complete, the trap was heated to 250°C for 2 minutes. During this time, contaminants were desorbed from the trap and immediately injected into the GC/FID#2.

The GC/FID#2 method for gas samples included an inlet temperature of 225°C and a detection temperature of 250°C, once again preventing condensation. For each sample, the initial oven temperature was 34°C, which was held constant for 0.5 minutes before being ramped at 10°C/minute to a final oven temperature of 65°C. This final temperature was held constant for 11 minutes, yielding a total run time of 14.6 minutes. The primary analytical column for GC/FID#2 was a Restek™ capillary column (30 m × 0.53 mm × 3.0 μm film thickness). Chromatographic peaks were drawn and integrated using HP GC ChemStation (Version Rev. A.04.02) software. A sample chromatogram for GC/FID#2 is shown in Figure 3-4, where the abscissa is time and the ordinate is the GC/FID response.

3.4.4. Gas Standards

A pressurized gas cylinder of known concentration of each chemical tracer was purchased (calibrated by Scott Specialty Gases, NIST traceable to Project 0454764). The cylinder contained a balance gas of air and was certified to contain: 40.0 ppm acetone, 50.6 ppm ethyl acetate, 40.5 ppm

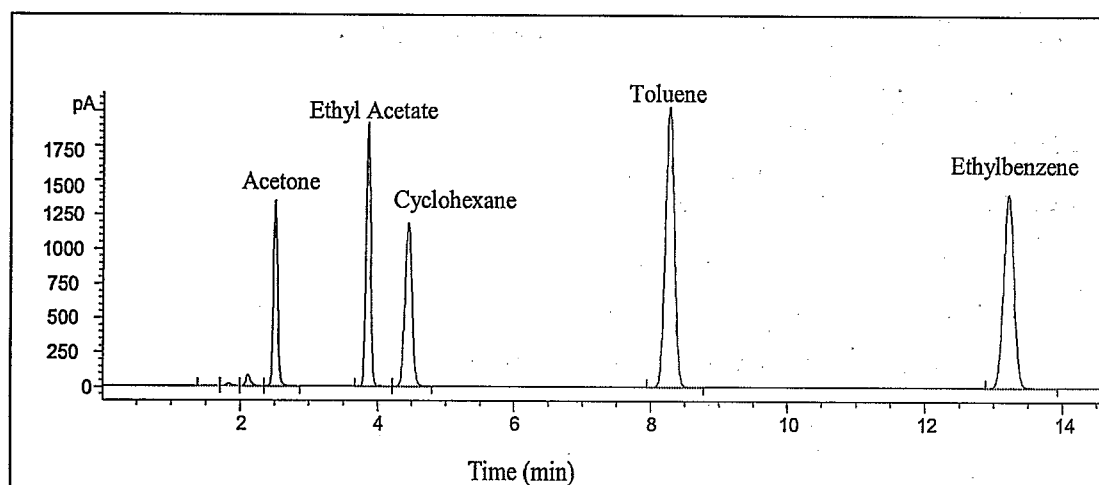


Figure 3-4. Gas sample chromatogram.

toluene, 27.7 ppm ethylbenzene, and 19.9 ppm cyclohexane. A 3 L Tedlar™ sample bag dedicated to gas standards was filled with the gas stock solution from the tank. A sampling configuration similar to the one shown in Figure 3-1 was used to draw the standard gas from the Tedlar™ bag through a clean sorbent tube. The volume of gas drawn through the tube was measured using a bubble flowmeter and a stopwatch. Different gas volumes were drawn through five sorbent tubes resulting in a five-point external calibration curve as shown in Figure 3-5. As with liquid standards, gas standards were prepared for each experiment in accordance with expected gas-phase measurements. External calibration curves for each tracer had a coefficient of determination (R^2) of at least 0.999.

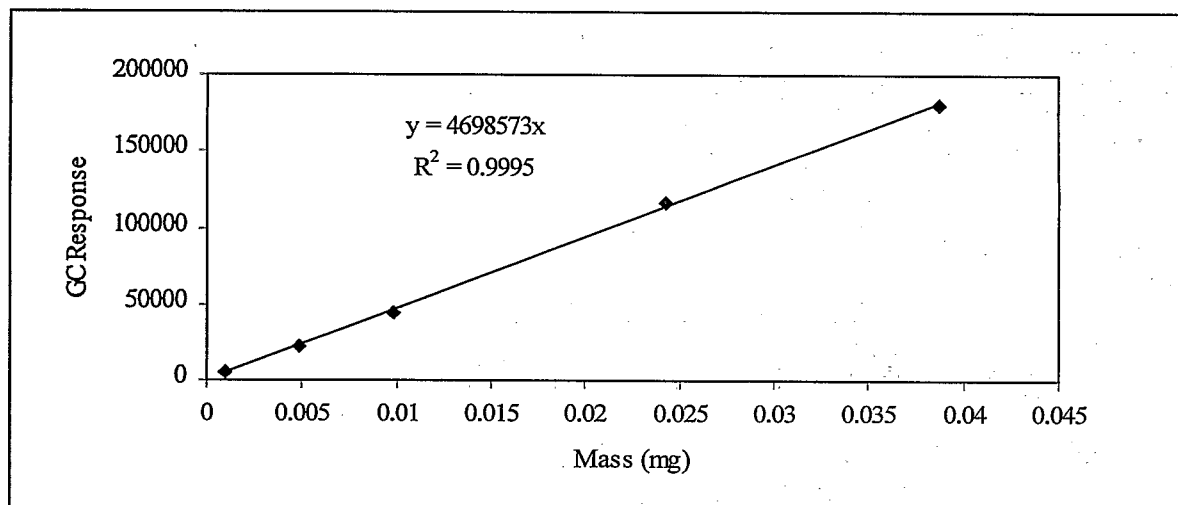


Figure 3-5. Gas-phase calibration curve for acetone.

3.5. QUALITY ASSURANCE MEASURES

A quality assurance plan was developed specifically for this project and was submitted to the US Environmental Protection Agency at an earlier date (September 1996). This plan was implemented throughout the entire study. A summary of quality assurance measures is given in this section.

3.5.1. Duplicate Samples

Because of the high volatility associated with several of the chemical tracers, duplicate liquid-phase samples were collected for every experiment. For the purposes of this study, duplicate samples refer to samples that were collected sequentially and that differed in time by fewer than 20 seconds. A summary of results associated with duplicate samples is presented in Table 3-2. The average difference reported in Table 3-2 includes all duplicates, even those that were removed for violating the quality assurance project plan.

The best duplication for liquid samples was achieved for ethyl acetate, with an average relative difference of 2.5%. Only 7.9% of all liquid sample duplicates had differences of greater than 20%. Twenty-six of the 38 liquid samples with poor duplication (>20% difference) were not included in the data analysis used to predict volatilization parameters. The remaining 12 duplicates had a relative difference between 22% and 36%, and were collected during the initial seconds of dishwasher experiments. As is explained in Chapter 5, chemicals rapidly volatilized from water used in a dishwasher within the first 45 seconds of operation. To characterize this drop in liquid-phase

Table 3-2. Duplicate sample results

Liquid Samples		
Compound	Number of Duplicates	Average Difference^a (%)
Acetone	113	3.1
Ethyl Acetate	67	2.5
Toluene	111	7.7
Ethylbenzene	101	8.2
Cyclohexane	96	13

^aDefined as $\frac{1}{n} \sum_{i=1}^n \frac{C_i - C_j}{\frac{C_i + C_j}{2}} \cdot 100$.

concentration, an initial value was needed. Dishwasher experiments using the average of these duplicates as initial concentrations are flagged in Chapter 5.

3.5.2. Replicate Experiments

Replicate experiments refer to experiments completed under approximately identical conditions, but not sequentially on the same day. For this study, 25% to 38% of experiments for each system were repeated. A summary of replicate experimental results is provided in Table 3-3.

Table 3-3 includes replicate experimental results for all sources. In fact, some replicate experiments for bathtubs and washing machine fill cycles were particularly poor for reasons that are explained later in this report. If those experiments are excluded from the analysis, the replicate sample results are improved significantly as presented in Table 3-4. The best replicate sample results were achieved for toluene, as shown in Table 3-4.

Table 3-3. Replicate sample results

Volatilization Parameters				
Compound	Average Difference ^a for η (%)	Median Difference ^a for η (%)	Average Difference ^b for $K_L A$ (%)	Median Difference ^b for $K_L A$ (%)
Acetone	38	30	26	19
Ethyl Acetate	23	26	26	27
Toluene	16	6.4	23	19
Ethylbenzene	18	6.9	22	17
Cyclohexane	20	5.0	28	19

^aDefined as $\frac{1}{n} \sum_{i=1}^n \frac{\eta_i - \eta_j}{\frac{\eta_i + \eta_j}{2}} \cdot 100$.

^bDefined as $\frac{1}{n} \sum_{i=1}^n \frac{K_L A_i - K_L A_j}{\frac{K_L A_i + K_L A_j}{2}} \cdot 100$.

Table 3-4. Replicate sample results excluding replicate experiments associated with filling

Volatilization Parameters				
Compound	Average Difference ^a for η (%)	Median Difference ^a for η (%)	Average Difference ^b for $K_L A$ (%)	Median Difference ^b for $K_L A$ (%)
Acetone	22	16	27	22
Ethyl Acetate	18	17	29	28
Toluene	6.1	4.2	17	12
Ethylbenzene	7.0	3.4	13	9.9
Cyclohexane	7.9	1.8	18	16

^aDefined as $\frac{1}{n} \sum_{i=1}^n \frac{\eta_i - \eta_j}{\frac{\eta_i + \eta_j}{2}} \cdot 100$.

^bDefined as $\frac{1}{n} \sum_{i=1}^n \frac{K_{L_i} A_i - K_{L_j} A_j}{\frac{K_{L_i} A_i + K_{L_j} A_j}{2}} \cdot 100$.

3.5.3. Experimental Blanks

A minimum of four analysis blanks were analyzed for every batch of experimental samples. These blanks were prepared in the laboratory and treated as an experimental sample through the analysis phase. The concentration of each volatile tracer in each blank was always below detection limit.

3.5.4. Method Detection Limit

The method detection limit was defined as:

$$MDL = t_{(n-1, 1-\alpha=0.95)} \cdot s_r \quad (3.6)$$

where

MDL = method detection limit

s_r = standard deviation of replicate analyses (M or M/L³)

$t_{(n-1, 1-\alpha=0.95)}$ = student's t value for a one-sided 95% confidence level and a standard deviation estimate (s_r) with $n-1$ degrees of freedom.

The MDLs were determined separately for liquid and gas samples. Results are listed in Table 3-5. It should be noted that the MDL test was completed for each GC/FID and column combination used in liquid and gas sample analyses. A majority of the liquid samples was analyzed using the 5 m column in GC/FID #1, and a majority of the gas samples was analyzed using the 30 m column in GC/FID #2. Less mass was used for each respective chemical to determine the MDLs for the 5 m column and GC/FID #2 than was used to determine the MDLs for the 30 m column and GC/FID #1. Subsequently, the standard deviation was lower for each chemical (s_p), resulting in a significantly lower associated MDL. If a lower mass had been used for the test with the 30 m column and GC/FID #2, the resulting MDLs would have been lower.

3.6. DATA ANALYSIS

Experimental systems with similar liquid flow patterns shared the same data analysis methods. The sources were grouped as follows:

1. Batch systems: dishwasher, washing machine (wash/rinse cycles), and bathtub (surface volatilization)
2. Plug-flow systems: shower and bathtub (flow-through)
3. Fill systems: washing machine (fill cycle) and bathtub (fill process)

The methods used to predict chemical stripping efficiencies, $K_L A$, k_g/k_l , and k_l and k_g for each type of experimental system are described below. The procedures in this section were applied independently for each chemical tracer. Thus, unless otherwise stated, five separate values were

Table 3-5. Method detection limits (MDLs) for liquid and gas samples

Chemical	Liquid MDL for 30 m column ^a (mg/L)	Liquid MDL for 5 m column ^a (mg/L)	Gas MDL for GC/FID #1 ^b (μ g)	Gas MDL For GC/FID #2 ^b (μ g)
Acetone	0.80	0.12	1.9	0.42
Ethyl Acetate	0.46	0.13	6.1	1.3
Toluene	0.23	0.09	4.0	1.2
Ethylbenzene	0.33	0.09	6.8	1.2
Cyclohexane	0.16	0.07	0.22	0.30

^aBoth 30 m and 5 m columns were used in GC/FID #1 for all liquid samples.

^bThe same 30 m column was used in both GC/FID #1 and GC/FID #2 for all gas samples.

reported for each volatilization parameter. Deviations from the solution techniques in this section are discussed in Chapters 4 to 7.

3.6.1. Chemical Stripping Efficiencies

Equations 2.1 and 2.2 were used to determine chemical stripping efficiencies for all experiments. For batch and fill systems, Equation 2.2 was used with $C_{l,end}$ equal to the final liquid-phase chemical concentration measurement, and $C_{l,init}$ equal to the measured liquid-phase chemical concentration before starting the experiment.

Equation 2.1 was used for the plug-flow systems, where $C_{l,in}$ was equal to the liquid-phase chemical concentration in the tracer reservoir and $C_{l,out}$ was equal to the liquid-phase chemical concentration in the specific system at the drain. When chemical volatilization in the tracer reservoir was a concern, that is, the inlet chemical concentration was changing, chemical stripping efficiencies were determined for several periods of the experiment. Each period consisted of at least one reservoir liquid-phase measurement and at least one system liquid-phase and gas-phase measurement. The stripping efficiency reported for the experiment was an average value based on each period.

3.6.2. Overall Mass Transfer Coefficients ($K_L A$)

In Section 2.3, mass balance models were developed for each experimental system. These models served as a way to determine $K_L A$ for each chemical tracer and source operating condition. Most of the models could not be solved analytically to determine $K_L A$. Thus, an iterative solution technique was adopted.

For batch systems, liquid-phase and gas-phase concentrations were predicted using Equations 2.23 and 2.24, respectively, for a given $K_L A$ value. For each experiment, liquid- and gas-phase chemical concentrations were measured at a given time. To determine the best $K_L A$ associated with these measurements, the mathematical models represented by Equations 2.23 and 2.24 were "fitted" with the best $K_L A$ value by minimizing the sum of squared normalized residuals between modeled and measured concentrations:

$$\text{Sum of square of residuals} = \sum \left(\frac{C_{\text{expt}} - C_m}{C_{\text{expt}}} \right)^2 \quad (3.7)$$

where

C_{expt} = experimentally measured liquid and gas concentrations (M/L³)

C_m = mathematically predicted liquid and gas concentrations (M/L³).

Equation 3.7 was minimized using two different approaches: (1) based on liquid-phase measurements only and (2) based on gas-phase measurements only.

An Excel™ Spreadsheet solver was used to complete the iterations. Ideally, the two best-fit values of $K_L A$ should be the same. However, as is explained in a later section, this often was not the case. Gas samples were collected for a longer sampling time than liquid samples. Because liquid samples were more representative of actual conditions at specific experimental times, they were used to predict values of $K_L A$. However, in some cases, the change in liquid-phase concentration for acetone and ethyl acetate was relatively small for the duration of an experiment. Thus, a general protocol was developed such that when overall stripping efficiencies for a given chemical approached the value of error associated with duplicate samples (see Table 3-2), associated values of $K_L A$ were based solely on gas-phase data. The solution techniques for each chemical are described in Chapters 4 to 7.

For fill systems, the differential mass balance equations (Equations 2.25 and 2.26) could not be solved analytically. Thus, a second-order Runge-Kutta numerical solution technique was used with 1-second time steps to determine the liquid- and gas-phase concentrations for a given value of $K_L A$. The second-order approximations of Equations 2.25 and 2.26 are predicted with the following equations:

$$C_l^{n+1} = C_l^n + \frac{\Delta t}{2} \{ f(t^n, C_l^n) + f[t^n + \Delta t, C_l^n + \Delta t f(t^n, C_l^n)] \} \quad (3.8)$$

$$C_g^{n+1} = C_g^n + \frac{\Delta t}{2} \{ f(t^n, C_g^n) + f[t^n + \Delta t, C_g^n + \Delta t f(t^n, C_g^n)] \} \quad (3.9)$$

where

C_1^{n+1} = chemical liquid-phase concentration at time step $n + 1$ (M/L^3)

C_1^n = chemical liquid-phase concentration at time step n (M/L^3)

Δt = differential time step (T)

$$f(t^n, C_1^n) = \left[\frac{Q_1 C_{1, \text{in}}}{V_1^n} - \frac{Q_1 C_1^n}{V_1^n} - \frac{K_L A C_1^n}{V_1^n} + \frac{K_L A C_g^n}{V_1^n H_c} \right]$$

$C_{1, \text{in}}$ = inlet liquid-phase chemical concentration (M/L^3)

Q_1 = liquid fill flowrate (L^3/T)

V_1^n = liquid volume at time step n (L^3) = $Q_1 \cdot t$

t = time (T)

K_L = overall mass transfer coefficient (L/T)

A = interfacial surface area between water and adjacent air (L^2)

H_c = Henry's law constant ($L^3_{\text{liq}}/L^3_{\text{gas}}$)

C_g^{n+1} = chemical gas-phase concentration at time step $n + 1$ (M/L^3)

C_g^n = chemical gas-phase concentration at time step n (M/L^3)

$$f(t^n, C_g^n) = \left[\frac{-Q_g C_g^n}{(V_t - V_1^n)} + \frac{Q_1 C_g^n}{(V_t - V_1^n)} + \frac{K_L A C_1^n}{(V_t - V_1^n)} - \frac{K_L A C_g^n}{(V_t - V_1^n) H_c} \right]$$

For plug-flow systems, $K_L A$ was determined by using Equation 3.7 with measured data and concentrations predicted by Equation 2.28 or Equation 2.30. Values of $K_L A$ were determined for different experimental periods and then averaged.

3.6.3. Ratio of Gas-to-Liquid Phase Mass Transfer Coefficients

An important component of this study involved the determination of k_g/k_l ratios for each experiment. Previous research has shown this ratio not to change significantly between chemicals for a given experimental system and operating conditions (Munz and Roberts, 1989). Thus, a single k_g/k_l value was estimated for each experiment, which was assumed to be constant for all chemicals. To determine this k_g/k_l value, the following steps were followed:

- For a given experiment, the value of $K_L A$ for each chemical was determined as outlined in Section 3.6.2.
- Using the experimentally determined values of $K_L A$, the ratio of $K_L A_i / K_L A_j$ for all combinations of chemicals ($K_L A_{\text{acetone}} / K_L A_{\text{ethyl acetate}}$, $K_L A_{\text{acetone}} / K_L A_{\text{toluene}}$, etc.) was calculated and organized in a 5×5 matrix (Matrix 1) as shown in Figure 3-6.
- The ratio of $K_L A_i / K_L A_j$ for each chemical combination was also predicted using Equation 2.15 (Ψ_m) and a single assumed value of k_g/k_l . These predicted ratios were organized in a second 5×5 matrix (Matrix 2) also following the format of Figure 3-6.
- Equation 3.7 was used to calculate the normalized residuals between the measured ratios of Matrix 1 and the predicted ratios of Matrix 2. These residuals were placed in the associated column and row position in a third 5×5 matrix (Matrix 3).
- All of the entries in Matrix 3 were summed to find the total residual between Matrix 1 and Matrix 2. The total residual was minimized by choosing different values of k_g/k_l used to predict $K_L A$ values in Matrix 2. The value of k_g/k_l which led to a minimum total residual between measured and predicted values was recorded and used for a given experiment.

$K_L A_i \backslash K_L A_j$	Acetone	Ethyl Acetate	Toluene	Ethylbenzene	Cyclohexane
Acetone	$\frac{K_L A_{\text{ace}}}{K_L A_{\text{ace}}} = 1$	$\frac{K_L A_{\text{ace}}}{K_L A_{\text{ea}}}$	$\frac{K_L A_{\text{ace}}}{K_L A_{\text{tol}}}$	$\frac{K_L A_{\text{ace}}}{K_L A_{\text{eb}}}$	$\frac{K_L A_{\text{ace}}}{K_L A_{\text{cyclo}}}$
Ethyl Acetate	$\frac{K_L A_{\text{ea}}}{K_L A_{\text{ace}}}$	$\frac{K_L A_{\text{ea}}}{K_L A_{\text{ea}}} = 1$	$\frac{K_L A_{\text{ea}}}{K_L A_{\text{tol}}}$	$\frac{K_L A_{\text{ea}}}{K_L A_{\text{eb}}}$	$\frac{K_L A_{\text{ea}}}{K_L A_{\text{cyclo}}}$
Toluene	$\frac{K_L A_{\text{tol}}}{K_L A_{\text{ace}}}$	$\frac{K_L A_{\text{tol}}}{K_L A_{\text{ea}}}$	$\frac{K_L A_{\text{tol}}}{K_L A_{\text{tol}}} = 1$	$\frac{K_L A_{\text{tol}}}{K_L A_{\text{eb}}}$	$\frac{K_L A_{\text{tol}}}{K_L A_{\text{cyclo}}}$
Ethylbenzene	$\frac{K_L A_{\text{eb}}}{K_L A_{\text{ace}}}$	$\frac{K_L A_{\text{eb}}}{K_L A_{\text{ea}}}$	$\frac{K_L A_{\text{eb}}}{K_L A_{\text{tol}}}$	$\frac{K_L A_{\text{eb}}}{K_L A_{\text{eb}}} = 1$	$\frac{K_L A_{\text{eb}}}{K_L A_{\text{cyclo}}}$
Cyclohexane	$\frac{K_L A_{\text{cyclo}}}{K_L A_{\text{ace}}}$	$\frac{K_L A_{\text{cyclo}}}{K_L A_{\text{ea}}}$	$\frac{K_L A_{\text{cyclo}}}{K_L A_{\text{tol}}}$	$\frac{K_L A_{\text{cyclo}}}{K_L A_{\text{eb}}}$	$\frac{K_L A_{\text{cyclo}}}{K_L A_{\text{cyclo}}} = 1$

Figure 3-6. Matrix format used to determine k_g/k_l .

3.6.4. Liquid- and Gas-Phase Mass Transfer Coefficients

Once the $K_L A$ values for each chemical and a single k_g/k_l value were determined for an experiment, liquid- and gas-phase mass transfer coefficients were calculated for each chemical. The overall resistance equation (Equation 2.5) was used to solve for $k_l A$, where $k_g A$ was written in terms of $k_l A$ using the k_g/k_l value. Once $k_l A$ was determined, the value for $k_g A$ was predicted. Although, k_g/k_l was constant for all chemical tracers, $k_l A$ and $k_g A$ were compound dependent.

3.7. FACTORIAL ANALYSIS

A factorial analysis was used to determine the main effects associated with the primary experimental variables (Box and Bisgaard, 1988). For dishwasher, washing machine wash/rinse cycle, and shower experiments, $2 \times 2 \times 2$ factorial arrays were designed. For these arrays, the main effect for a single variable was calculated as the average of the difference between responses at two levels of the factor of interest. Variable responses were in terms of stripping efficiencies and $K_L A$ values. This procedure was completed for all three factorial variables. The largest positive or negative value corresponded to the largest main effect.

3.8. MASS CLOSURE ASSESSMENT

Previous research related to the volatilization of chemicals from drinking water, in particular showers, has suffered from poor mass closure and, in some cases, lack of adequate experimental measurements to assess mass closure. Therefore, an important protocol for each source experiment was to obtain adequate mass closure. Mass closure for batch systems was determined using:

$$\% \text{ mass recovered} = \frac{V_l C_{l,2} + V_g C_{g,2} + Q_g \int_{t_1}^{t_2} C_g dt}{V_l C_{l,1} + V_g C_{g,1}} \quad (3.10)$$

where

V_l = liquid volume (L^3)

V_g = headspace volume (L^3)

$C_{l,1}$ = chemical concentration in liquid phase at time 1 (M/L^3)

$C_{l,2}$ = chemical concentration in liquid phase at time 2 (M/L^3)

$C_{g,1}$ = chemical concentration in gas phase at time 1 (M/L^3)

$C_{g,2}$ = chemical concentration in gas phase at time 2 (M/L^3)

Q_g = ventilation rate of system (L^3/T)

t_1 = time 1 (T)

t_2 = time 2 (T).

For fill systems, mass closure was determined by:

$$\% \text{ mass recovered} = \frac{V_l C_{l,2} + V_g C_{g,2} + Q_g \int_{t_1}^{t_2} C_g dt}{Q_l C_{l,in} (t_2 - t_1) + V_g C_{g,1}} \quad (3.11)$$

where

V_l = liquid volume (L^3)

V_g = headspace volume (L^3)

$C_{l,in}$ = inlet chemical concentration (M/L^3)

$C_{l,2}$ = chemical concentration in liquid phase at time 2 (M/L^3)

$C_{g,1}$ = chemical concentration in gas phase at time 1 (M/L^3)

$C_{g,2}$ = chemical concentration in gas phase at time 2 (M/L^3)

Q_l = liquid flowrate in and out of system (L^3/T)

Q_g = ventilation rate of system (L^3/T)

t_1 = time 1 (T)

t_2 = time 2 (T).

Finally, for plug-flow systems, the following mass closure equation was used:

$$\% \text{ mass recovered} = \frac{Q_l \int_{t_1}^{t_2} C_{l,out} dt + V_g C_{g,2} + Q_g \int_{t_1}^{t_2} C_g dt}{Q_l C_{l,in} (t_2 - t_1) + V_g C_{g,1}} \quad (3.12)$$

where

V_g = headspace volume (L^3)

$\bar{C}_{l,in}$ = average chemical concentration measured in tracer reservoir (M/L³).

$C_{l,out}$ = chemical concentration in liquid phase at outlet (M/L³)

C_g = chemical concentration in gas phase (M/L³)

$C_{g,1}$ = chemical concentration in gas phase at time 1 (M/L³)

$C_{g,2}$ = chemical concentration in gas phase at time 2 (M/L³)

Q_l = liquid flowrate in and out of system (L³/T)

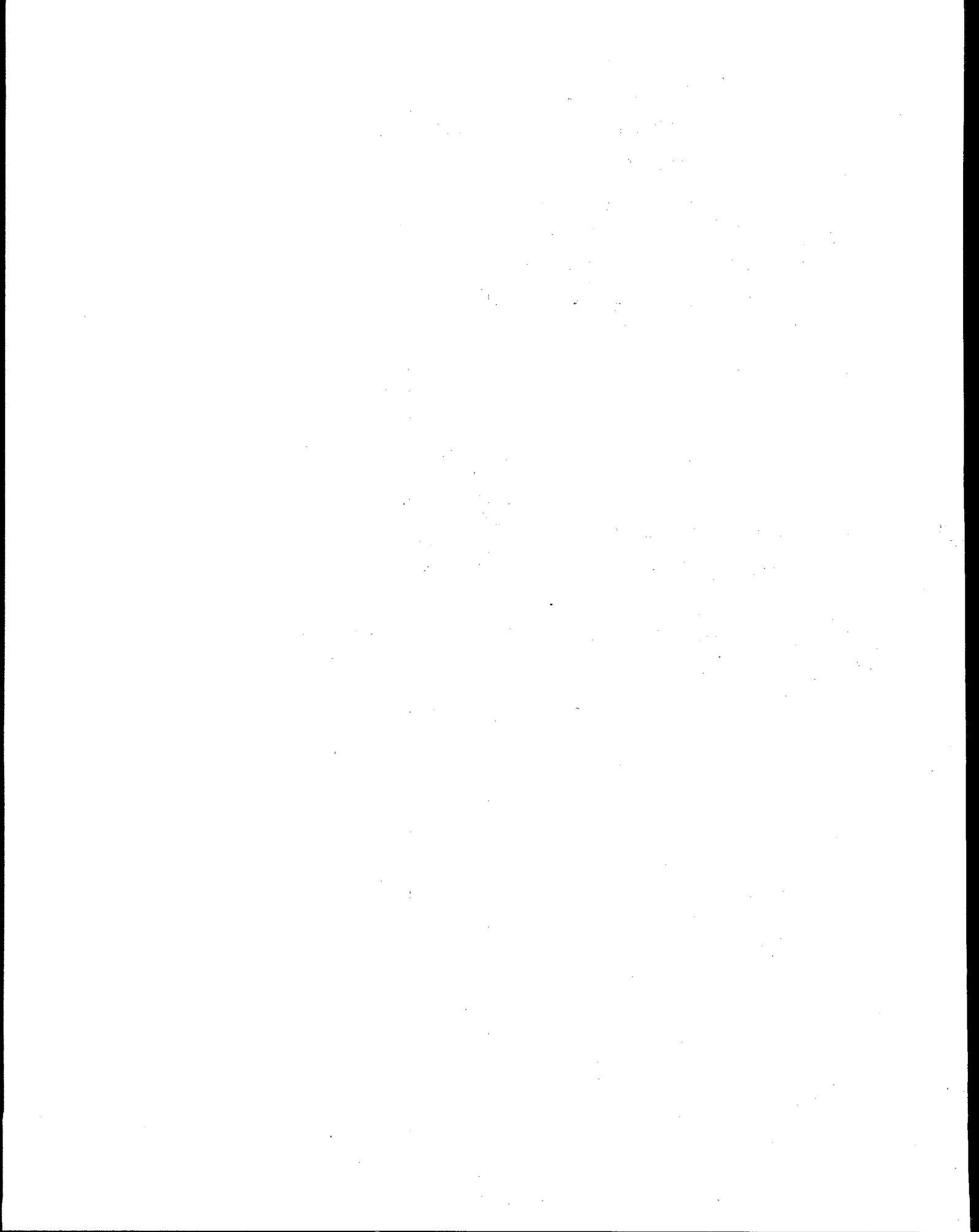
Q_g = ventilation rate of system (L³/T)

t_1 = time 1 (T)

t_2 = time 2 (T).

For most experimental systems, C_g was measured at several times during an experiment. In these cases, there were periods where the exact gas concentration in the system's headspace was not known. To account for these unknown values in Equations 3.10 to 3.12, the concentrations of samples collected on either side of this period were averaged.

Mass closure results for all chemicals are reported in each respective source section. Adequate mass closure was defined as 75% to 125%.



4. SHOWER EXPERIMENTS

Shower operation consists of a single water activity, that is, no separate cycles. To study this activity, a wide range of operating conditions were applied to a consistent experimental design.

4.1. EXPERIMENTAL SYSTEM

A 140 cm × 70 cm × 178 cm (1.7 m³ total volume) shower stall (with bathtub) was purchased to complete all shower experiments. The shower stall was installed in the stainless steel chamber on a 58 cm high cinder-block platform. The platform served two purposes: (1) it elevated the system to an appropriate height for draining and collecting liquid samples and (2) it elevated the shower stall such that it reached the stainless steel chamber's ceiling, which provided a system boundary. Other system boundaries included three walls and a floor made of fiberglass coated with an unknown plastic, and one wall (a curtain) made of Tedlar™.

Showering involves production of a spray of water that impacts on and cascades down surfaces to the bathtub floor. The floor slopes toward a drain where water is removed from the system. The experimental shower system required an auxiliary water supply (see Figure 4-1). To meet this need, the washing machine described in Section 6.1.1 effectively served as a tracer reservoir. The washing machine was directly plumbed to the building cold and hot water supply. Chemicals were added to the washing machine as it filled (~ 90 L). The reservoir's contents were further mixed by using wash cycle agitation. The washing machine contents were pumped with a rotary vane pump (PROCON™) through 1.3 cm OD Teflon™ tubing to the shower head. An adjustable low-flow (9.5 L/minute maximum) showerhead (Interbath™) was used for all experiments. The showerhead could be adjusted between fine and coarse spray. A 60 mm, 19 L/min maximum rotameter (King Instrument Co.) was installed in the Teflon™ tubing line to measure the liquid flowrate through the system. The experimental flowrates were based on typical values and the restrictions of the showerhead. The accuracy of the rotameter was verified by timing the collection of a known volume of liquid from the showerhead.

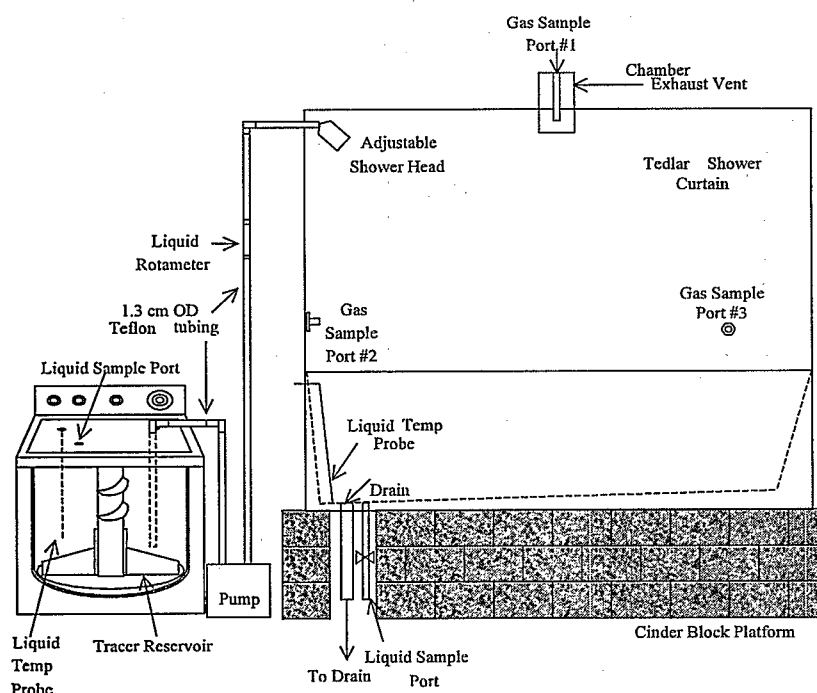


Figure 4-1. Shower experimental system.

Liquid samples were collected from the washing machine reservoir in a manner similar to the actual washing machine experiments (see Section 6.1.1). The shower stall was designed to collect the necessary samples to solve the shower mass balance equations (Equations 2-28 and 2-30). A liquid sample port was installed in the base of the bathtub near the drain. A 30 cm length of 0.64 cm OD Teflon™ tubing with a Teflon™ sample valve was connected to this port. Liquid samples were collected as described in Section 3.3.1.

Three gas sample ports were installed in the system to better understand the gas-phase chemical concentration distribution in the stall. Sample port #1 was located within the chamber exhaust vent and consisted of a 91-cm-long 0.64 cm OD Teflon™ tube attached to a stainless steel Swagelok™ union at which point a sorbent tube was connected. Port #2 was a bore-through Swagelok™ fitting located on the wall with the showerhead, 53 cm from the bathtub floor. Port #3 was located on the shower curtain, 61 cm from the floor of the bathtub. A Swagelok™ fitting was inserted in the curtain for sample collection. Because of time constraints, only gas samples collected from sample ports #1 and #3 were collected as described in Section 3.3.2. The

sampling flowrates for sorbent tubes used for sample collection at port #2 were measured and recorded before the start of each experiment with clean air. Thus, a bubble flowmeter was not used in the sampling train (see Figure 3-1) at this port.

A liquid temperature probe was submerged in the tracer reservoir, and a second probe was inserted in the shower stall near the drain. Liquid temperatures at these two locations were continuously measured using a thermocouple and digital monitor. The temperature difference between these two points was minimal for all experiments.

4.2. EXPERIMENTAL DESIGN

The following operating variables were selected for shower experiments: water temperature, liquid flowrate, and shower spray type. The impact of these operating conditions on chemical volatilization rates was studied using a $2 \times 2 \times 2$ factorial array. As shown in Figure 4-2, variable ranges were cold ($T \approx 22^\circ\text{C}$) versus warm ($T \approx 35^\circ\text{C}$), low liquid flowrate (6.1 L/minute) versus high liquid flowrate (9.1 L/minute), and fine shower spray versus coarse shower spray. Eight experiments were completed, with two additional experiments serving as replicates.

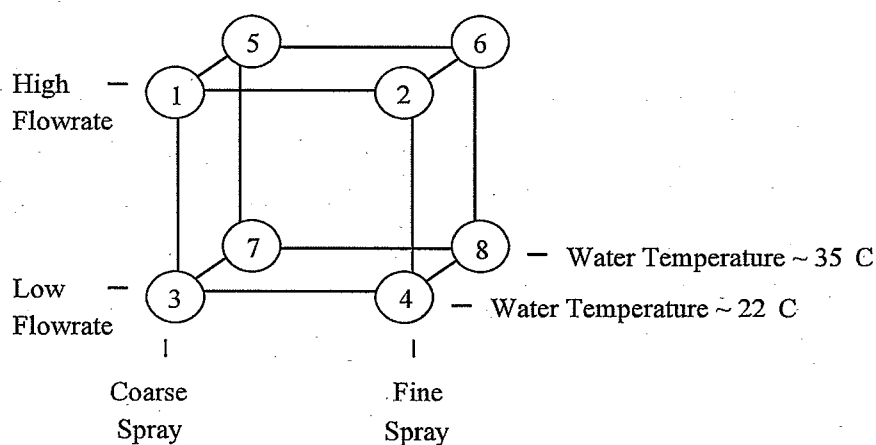


Figure 4-2. Shower factorial experimental design.

4.3. SOURCE-SPECIFIC METHODOLOGY

Prior to each shower experiment, the following tasks were completed:

- Flowrates for sorbent tubes used at port #2 were measured with clean air
- The desired experimental liquid flowrate was set using the rotameter
- The tracer reservoir (washing machine) was filled with either cold or warm tap water
- The chemical tracer solution was pumped into the washing machine as it filled
- The washing machine reservoir solution was mixed by allowing the washing machine to agitate for approximately 1 minute
- An initial gas-phase sample was collected from sample port #1 in the shower stall
- Two initial reservoir liquid-phase samples were collected.

4.3.1. Sample Schedule

Shower experiments lasted 8 minutes, during which time liquid-phase samples were collected from both the tracer reservoir and the shower stall. Five shower stall liquid samples were collected at experimental times of 0.5, 1.5, two at 3.75, and 7.75 minutes. Although the tracer reservoir chemical concentrations did not change significantly for most experiments, three tracer reservoir samples and one duplicate sample were collected and scheduled within 45 seconds of each shower stall sample so that several independent stripping efficiencies could be determined for a single experiment.

A total of 12 gas samples were collected for every shower experiment. Six gas samples were collected at port #1 for 30 seconds and were scheduled such that a shower stall liquid sample was collected at the midpoint of the gas sample time. Three gas samples were collected at each port #2 and port #3. The sampling times at these ports were scheduled to occur simultaneously, as well as at the same time as a gas sample collected at port #1. Thus, the gas-phase chemical concentration distribution was determined for three separate time periods in an experiment. Finally, a gas sample was collected after the experiment had ended and no water flowed through the system. The start time of this sample ranged from 5 to 20 minutes after the completion of an experiment. The gas collection time was 5 minutes.

4.3.2. Ventilation Rate

Through use of a smoke test, it was determined that gas primarily exited the chamber through the 10 cm exhaust port. Plastic dryer hose was sealed to the chamber exhaust port and was connected to a 76 cm length of straight PVC pipe. An anemometer was used to measure the velocity in this 8.3 cm ID pipe. The system ventilation rate (Q_g) was calculated using the cross-sectional area of the pipe (54 cm^2) and the measured velocity. The air exchange rate was determined by dividing the system's ventilation rate by the system volume. The shower system was well ventilated, with air exchange rates ranging from 12 to 13 air changes per hour (ACH). The specific air exchange rate for each experiment was measured during the actual experiment.

4.3.3. Parameter Estimation

Each shower experiment was divided into three periods: initial (0 to 1 minute), intermediate (3.5 to 4.5 minutes), and final (5.75 to 8 minutes). During each period, at least one tracer reservoir liquid sample, shower outlet sample, and shower gas sample were collected. Chemical stripping efficiencies and values of $K_L A$ were determined for each time period and averaged, respectively, to obtain final values. Ratios of k_g/k_l , $k_l A$, and $k_g A$ were estimated based on averaged values of $K_L A$ for each chemical.

4.4. SHOWER RESULTS

Based on the experimental methodology presented in Sections 3.0 and 4.3, the overall chemical stripping efficiencies and mass transfer coefficients ($K_L A$, $k_l A$, and $k_g A$) for 10 shower experiments are presented in this chapter. In addition, the effects of liquid temperature, liquid flowrate, shower spray type, and chemical properties on each response are discussed. The determination of k_g/k_l values and associated implications are also presented.

The operating conditions for each experiment are listed in Table 4-1.

4.4.1. Chemical Stripping Efficiencies

Stripping efficiencies for each experimental chemical are presented in Tables 4-2 to 4-6, respectively. Stripping efficiencies were based on liquid-phase measurements collected from the tracer reservoir and shower outlet drain. In addition to chemical stripping efficiencies, Tables 4-2 to 4-6 provide the results of the factorial main effect analysis (see Section 3.7 for

Table 4-1. Shower experiment operating conditions

Experiment #	Liquid temperature (°C)	Liquid flowrate (L/min)	Gas flowrate (L/min)	ACH (1/hr)	Spray type
1	21	9.1	370	13	Coarse
2	22	9.1	343	12	Fine
3	21	6.1	360	12	Coarse
4	22	6.1	358	12	Fine
5	35	9.1	379	13	Coarse
6	34	9.1	354	12	Fine
6 replicate	34	9.1	373	13	Fine
7	36	6.1	364	13	Coarse
8	35	6.1	371	13	Fine
8 replicate	34	6.1	367	13	Fine

methodology). The three factors of the shower experimental two-level factorial arrays were shower spray type, liquid flowrate, and liquid temperature. As explained in Section 3.7, the main effect for a single variable was calculated as the average of the differences between responses at two levels of the factor of interest. For example, the shower spray effect on acetone's stripping efficiency may be calculated as:

Corresponding experiments:		Difference in stripping efficiencies
1 - 2	=	-2.1 %
3 - 4	=	-0.2 %
5 - Average (6 and 6 replicate)	=	1.0%
7 - Average (8 and 8 replicate)	=	-1.0%
Average	=	-0.075%

As shown in Table 4-2, the difference in experimental response was listed twice, once for each corresponding experiment. Duplicating the listing of each difference in response, however, does not affect the average value for each variable. The experimental results for Experiments 6 and 6 replicate and Experiments 8 and 8 replicate were averaged, respectively, before applying factorial analyses. Tables 4-3 to 4-6 follow this same format.

Table 4-2. Acetone stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect ^a (%)	Liquid flowrate effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	High	Coarse	6.3	-2.1	-2.8	6.7
2	Cold	High	Fine	8.4	-2.1	-0.90	3.6
3	Cold	Low	Coarse	9.1	-0.20	-2.8	6.9
4	Cold	Low	Fine	9.3	-0.20	-0.90	5.7
5	Warm	High	Coarse	13	1.0	-3.0	6.7
6	Warm	High	Fine	11	1	-3.0	3.6
6 rep.	Warm	High	Fine	12			
7	Warm	Low	Coarse	16	1.0	-3.0	6.9
8	Warm	Low	Fine	14	1	-3.0	5.7
8 rep.	Warm	Low	Fine	15			
				Average =	-0.075	-2.4	5.7

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-3. Ethyl acetate stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect ^a (%)	Liquid flowrate effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	High	Coarse	15	0	-5.0	12
2	Cold	High	Fine	15	0	-5.0	14
3	Cold	Low	Coarse	20	0	-5.0	12
4	Cold	Low	Fine	20	0	-5.0	15
5	Warm	High	Coarse	27	-2.0	-5.0	12
6	Warm	High	Fine	28	-2.0	-6.0	14
6 replicate	Warm	High	Fine	29			
7	Warm	Low	Coarse	32	-3.0	-5.0	12
8	Warm	Low	Fine	33	-3.0	-6.0	15
8 replicate	Warm	Low	Fine	36			
				Average =	-1.3	-5.3	13

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-4. Toluene stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect ^a (%)	Liquid flowrate effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	High	Coarse	61	-7.0	-2.0	7.0
2	Cold	High	Fine	68	-7.0	4.0	7.0
3	Cold	Low	Coarse	63	-1.0	-2.0	11
4	Cold	Low	Fine	64	-1.0	4.0	11
5	Warm	High	Coarse	68	-7.0	-6.0	7.0
6	Warm	High	Fine	75	-7.0	0	7
6 replicate	Warm	High	Fine	74			
7	Warm	Low	Coarse	74	-1.0	-6.0	11
8	Warm	Low	Fine	73	-1.0	0	11
8 replicate	Warm	Low	Fine	77			
				Average =	-4.0	-1.0	9.0

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-5. Ethylbenzene stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect ^a (%)	Liquid flowrate effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	High	Coarse	62	-6.0	-1.0	6.0
2	Cold	High	Fine	68	-6.0	5.0	7.0
3	Cold	Low	Coarse	63	0	-1.0	10
4	Cold	Low	Fine	63	0	5.0	11
5	Warm	High	Coarse	68	-7.0	-5.0	6.0
6	Warm	High	Fine	75	-7.0	1	7
6 replicate	Warm	High	Fine	74			
7	Warm	Low	Coarse	73	-1.0	-5.0	10
8	Warm	Low	Fine	72	-1.0	1	11
8 replicate	Warm	Low	Fine	75			
				Average =	-3.5	0	8.5

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-6. Cyclohexane stripping efficiencies for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	Stripping efficiency (%)	Shower spray effect ^a (%)	Liquid flowrate effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	High	Coarse	65	-8.0	-1.0	10
2	Cold	High	Fine	73	-8.0	7.0	4.0
3	Cold	Low	Coarse	66	0	-1.0	10
4	Cold	Low	Fine	66	0	7.0	12
5	Warm	High	Coarse	75	-2.0	1.0	10
6	Warm	High	Fine	77			4
6 replicate	Warm	High	Fine	77	-2.0	-1.0	
7	Warm	Low	Coarse	76	-2.0	1.0	10
8	Warm	Low	Fine	75			12
8 replicate	Warm	Low	Fine	80	-2.0	-1.0	
				Average =	-3.0	1.0	9.0

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Stripping efficiencies for acetone ranged from 6.3% to 16%, with the highest value for the conditions of warm water, low liquid flowrate, and coarse shower spray. The single variable with the largest effect on acetone's stripping efficiency was liquid temperature, with a main effect of 5.7%. The main effect due to differences in liquid temperature, was calculated by subtracting cold water stripping efficiencies from corresponding warm water stripping efficiencies. Thus, 5.7% indicates an absolute increase in stripping efficiency with higher temperature water. The shower experiments were grouped according to similar liquid temperature, and the following stripping efficiencies resulted: 8.3% for cold water experiments (Experiments 1 to 4), and 14% for warm water experiments (Experiments 5 to 8 replicate). This result was expected, owing to the increase in Henry's law constant with increasing temperature.

For the temperatures listed in Table 4-1, Henry's law constants for acetone ranged from 0.0010 $\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (21°C, Experiments 1 and 3) to 0.0023 $\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (36°C, Experiment 7).

The second highest main effect involved liquid flowrate with a value of -2.4%. The liquid flowrate effect was determined by the difference in high flowrate and low flowrate stripping efficiencies, so a negative effect indicates an increase in stripping efficiency at low flowrates. At lower shower flowrates, a liquid droplet has a longer residence time in the shower stall, which may

lead to higher chemical volatilization. The experiments were grouped according to liquid flowrate and temperature, and the following average stripping efficiencies were calculated: 7.4% for high flowrate and cold water (Experiments 1 and 2), 9.2% for low flowrate and cold water (Experiments 3 and 4), 12% for high flowrate and warm water (Experiments 5, 6, and 6 replicate), and 15% for low flowrate and warm water (Experiments 7, 8, and 8 replicate). Shower spray had a less significant impact on acetone stripping efficiencies.

Shower Experiments 6 and 8 were replicated. The acetone stripping efficiencies for these two experiments were compared and the following relative differences calculated: 8.7% for Experiments 6 and 6 replicate, and 6.9% for Experiments 8 and 8 replicate.

Ethyl acetate stripping efficiencies ranged from 15% to 36% (see Table 4-3). As with acetone, the highest value corresponded to the conditions of warm water and low flowrate. However, unlike acetone, the highest stripping efficiency for ethyl acetate occurred during fine spray conditions. The variable with the highest main effect on ethyl acetate's stripping efficiency was liquid temperature, with a value of 13%. Ethyl acetate stripping efficiencies were grouped according to liquid temperature, and the following average values calculated: 18% for cold water experiments and 31% for warm water experiments. Again, increasing the water temperature increased ethyl acetate's Henry's law constant, resulting in significantly higher stripping efficiencies. The Henry's law constant effect is also evident when comparing acetone and ethyl acetate stripping efficiencies for similar experimental conditions. In all cases, ethyl acetate, which has a higher Henry's law constant, had higher stripping efficiencies than acetone. For the temperatures listed in Table 4-1, Henry's law constants (H_c) for ethyl acetate ranged from $0.0041 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (21°C, Experiments 1 and 3) to $0.0080 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (36°C, Experiment 7), that is, approximately four times that of acetone.

With a main effect value of -5.3%, liquid flowrate had less than half the impact of water temperature on ethyl acetate stripping efficiency. When experiments were grouped according to liquid flowrate and water temperature, the following average values resulted: 15% for cold water and high flowrate experiments, 20% for cold water and low flowrate experiments, 28% for warm water and high flowrate experiments, and 34% for warm water and low flowrate experiments. Again, shower spray had a less significant main effect on ethyl acetate's stripping efficiency.

For the two replicate experiments, Experiments 6 and 8, the following relative differences were determined: 3.5% for Experiment 6 and Experiment 6 replicate, and 8.7% for Experiment 8 and Experiment 8 replicate.

As shown in Table 4-4, toluene stripping efficiencies ranged from 61% to 77%. As expected, the highest toluene stripping efficiencies resulted when warm water was used. The main effect for liquid temperature was 9.0%. Experiments using cold water had an average stripping efficiency of 64%, and experiments using warm water had an average stripping efficiency of 74%. The gap between the cold water average stripping efficiency and warm water average stripping efficiency was much narrower than for acetone and ethyl acetate. For the temperatures listed in Table 4-1, Henry's law constants for toluene ranged from $0.24 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (21°C, Experiments 1 and 3) to $0.38 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (36°C, Experiment 7).

The second largest main effect for toluene stripping efficiencies, unlike those for acetone and ethyl acetate, was the type of shower spray, with a value of -4.0%. Interestingly, the magnitude of the shower spray, main effect was highly dependent on liquid flowrate. The difference in stripping efficiency between shower spray types at high flowrates was -7.0%, but at low flowrates the difference was only -1.0%. Interaction between these two variables is likely to influence the magnitude of a chemical's liquid-phase mass transfer coefficient (k_l). Thus, the associated effects of liquid flowrate and shower spray will have the greatest effect on chemicals dominated by liquid-phase resistance to mass transfer (toluene, ethylbenzene, and cyclohexane). Toluene stripping efficiencies were grouped according to the two largest main effects, water temperature and shower spray type, and the following average values were calculated: 62% for cold water and coarse spray (Experiments 1 and 3), 66% for cold water and fine spray (Experiments 2 and 4), 71% for warm water and coarse spray (Experiments 5 and 7), and 75% for warm water and fine spray (Experiments 6, 6 replicate, 8, and 8 replicate).

Replicate experimental results led to a 1.3% relative difference in toluene stripping efficiencies for Experiments 6 and 6 replicate, and 5.3% relative difference for Experiments 8 and 8 replicate.

Ethylbenzene stripping efficiencies ranged from 62% to 75% (see Table 4-5). This range was similar in magnitude to the range of stripping efficiencies reported for toluene. As discussed in Section 3.2.1, toluene and ethylbenzene have similar Henry's law constants (for the temperatures listed in Table 4-1, ethylbenzene has Henry's law constants between $0.26 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ and $0.57 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$), and thus should yield similar volatilization results. On an experiment-by-experiment basis, toluene and ethylbenzene stripping efficiencies were nearly identical. The largest relative deviation in stripping efficiencies for the two compounds was less than 3% (Experiment 8 replicate). It should also be noted that the stripping efficiencies for toluene and ethylbenzene were significantly higher than those observed for acetone and ethyl acetate. Again, an increase in Henry's law constant led to an increase in chemical stripping efficiencies.

As expected, ethylbenzene had main effects similar to those of toluene. Grouping stripping efficiencies based on water temperature yielded the following averages: 64% for cold water experiments and 73% for warm water experiments. Separating the liquid temperature groups to account for shower spray type resulted in the following average values: 63% for cold water and coarse spray, 66% for cold water and fine spray, 71% for warm water and coarse spray, and 74% for warm water and fine spray.

Relative differences in stripping efficiency for replicate experiments were 1.3% for Experiments 6 and 6 replicate, and 4.1% for Experiments 8 and 8 replicate.

Finally, cyclohexane stripping efficiencies ranged from 65% to 80% (see Table 4-6). For similar experimental conditions, cyclohexane consistently had the highest stripping efficiency of the five experimental tracers. The largest main effect was liquid temperature with a value of 9.0%. Following the format for previous tracers, the average cold water stripping efficiency was 68%, and the average warm water stripping efficiency was 77%. Similar to toluene and ethylbenzene, shower spray type had the second highest main effect with a value of -3.0%. Experimental results were regrouped according to shower spray type and water temperature, and the following averages were calculated: 66% for cold water and coarse spray, 70% for cold water and fine spray, 76% for warm water and coarse spray, and 77% for warm water and fine spray. This second regrouping did not yield results significantly different from the first set of averages for cold and warm water,

and was thereby unnecessary. For the temperatures listed in Table 4-1, Henry's law constants for cyclohexane ranged from $6.3 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (21°C, Experiments 1 and 3) to $10 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (36°C, Experiment 7).

Unlike the other chemical tracers, the liquid flowrate main effect on cyclohexane's stripping efficiencies was positive, indicating a decrease in stripping efficiency with decreasing flowrate. A specific reason for this trend could not be identified.

Replicate experimental stripping efficiencies had a relative difference of 0% for Experiments 6 and 6 replicate and 6.5% for Experiments 8 and 8 replicate.

An attempt was made to compare the chemical stripping efficiencies described above with those reported by other researchers who used similar operating conditions and chemical tracers. A summary of previous research related to volatilization in showers was presented in a Phase I report to EPA as part of this project (Corsi et al., 1996) and are also given in the database in the Appendix. Additional papers have been reviewed since the Phase I report was submitted (*e.g.*, Giardino and Andelman [1996]), and all of these have been added to the database.

Previous researchers have not studied chemicals with Henry's law constants as low as acetone. Thus, the results described herein are unique for this compound and extend the range of chemical volatilities to values much lower than those previously reported.

Overall, Giardino and Andelman (1996) used operating conditions most similar to those in this study and will serve as the primary basis of comparison. Giardino and Andelman studied emissions of trichloroethene (TCE), chloroform (CHCl_3), and 1,2-dibromo-3-chloropropane (DBCP) in a 1.5 m^3 experimental shower. As in the results of this study, they determined that water temperature had a dominant effect on the total release of each tracer chemical.

Giardino and Andelman's Experiment 17 included an air exchange rate of 12.3/hour, water flowrate of 5 L/minute, and water temperature of 30°C. For these conditions, the stripping efficiency of DBCP, which has the lowest Henry's law constant of any chemical tested to date for showers, was only 17%. For this study, Experiment 8 replicate included operating conditions

similar to those reported above (air exchange rate = 13/hour; water flowrate = 6.1 L/minute; water temperature = 34°C). The corresponding stripping efficiency for ethyl acetate, a chemical with a Henry's law constant at 34°C (slightly lower than that of DBCP at 30°C), was over twice (36%) the value reported by Giardino and Andelman for DBCP. Ethyl acetate's Henry's law constant is similar to that of DBCP, and thus differences in stripping efficiency between DBCP and ethyl acetate cannot be accounted for entirely by water temperature. Differences are likely due to differences in commercial showerheads that were used, as well as subsequent differences in droplet sizes and velocities.

Giardino and Andelman (1996) also studied TCE, which has a Henry's law constant approximately 25% greater than that for ethylbenzene, at 22°C. Thus, TCE would be expected to have slightly greater stripping efficiencies for similar operating conditions. Giardino and Andelman reported a TCE stripping efficiency of 60% for their Experiment 2 (air exchange rate = 10.8/hour; water flowrate = 5.1 L/minute; water temperature = 22°C). In this study, the stripping efficiency for ethylbenzene was slightly higher (63%) for similar conditions (Experiment 3; air exchange rate = 12/hour; water flowrate = 6.1 L/minute; water temperature = 21°C). For a second experiment involving a higher water flowrate (10 L/minute), Giardino and Andelman observed a TCE stripping efficiency of 57%. For similar experimental conditions (Experiments 1 and 2 of this study), the stripping efficiency for ethylbenzene was observed to be 62% (coarse spray) and 68% (fine spray). In an earlier study, Giardino et al. (1992) observed TCE stripping efficiencies of 59% to 67% for similar operating conditions.

McKone and Knezovich (1991) also studied stripping efficiencies for TCE in an experimental shower. One of their operating conditions (air exchange rate = 12/hour; liquid flowrate = 9.5 L/minute; water temperature = 22°C) was nearly identical to those used in Experiments 1 and 2 of this study. The stripping efficiency for TCE was reported to be 58%, consistent with Giardino and Andelman (1996) and Giardino *et al.* (1992), and slightly lower than those obtained for ethylbenzene in this study. The differences in stripping efficiencies between TCE and ethylbenzene could easily be caused by differences in hydrodynamic conditions associated with water flowrate and shower configurations, as well as experimental errors associated with each study.

Finally, several researchers used chemicals with relatively high Henry's law constants ($> 2.0 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$) in shower experiments. It was expected that these higher volatility chemicals would have similar stripping efficiencies because of the associated insignificance of gas-phase resistance to mass transfer. For example, Bernhardt and Hess (1995) studied stripping efficiencies for radon in household showers. Radon has a slightly lower Henry's law constant than cyclohexane, but both compounds should be dominated by liquid-phase resistance to mass transfer. For a water temperature of 23°C and liquid flowrate of 5.7 L/minute (gas exchange rate in the shower stall was not measured), the stripping efficiency for radon was reported to be 78%. For similar operating conditions (Experiments 3 and 4 of this study), the stripping efficiency for cyclohexane was determined to be 66%. The range of radon stripping efficiencies reported by Bernhardt and Hess was 57% to 88%. Cyclohexane stripping efficiencies for this study ranged from 65% to 80%.

At liquid flowrates of 2 to 4 L/minute, Giardino and Hageman (1996) measured radon stripping efficiencies ranging from 67% to 70%. Studies with unknown operating parameters led to observed radon stripping efficiencies of 63% to 71% (Gesell and Prichard, 1980; Hess et al., 1982; Hopke et al., 1995; Partridge, 1979).

Tancrede et al. (1992) measured the stripping efficiencies of five experimental chemicals including carbon tetrachloride (CCl_4), which has a Henry's law constant of $2.3 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ at 42°C . The chemical stripping efficiency for CCl_4 was 59% at a liquid flowrate of 9.7 L/minute and 77% for a liquid flowrate of 13 L/minute . Again, these results are consistent with those observed for other chemicals with relatively high Henry's law constants.

It is clear from this study, as well as several others reported in the literature, that for the same operating conditions stripping efficiency increases with increasing Henry's law constant. It is also evident that chemicals of sufficiently high Henry's law constant have comparable stripping efficiencies for similar operating conditions. Because the conditions used in this study should represent a reasonable spectrum of those associated with residential showering, an average stripping efficiency was determined for each chemical tracer and is plotted in Figure 4-3 as a function of Henry's law constant at 25°C . This plot may be used as a screening tool for

approximating chemical stripping efficiencies, given knowledge of that chemical's Henry's law constant at 25°C, the temperature for which Henry's law constants are most widely reported. The best-fit line associated with the averaged data in Figure 4-3 stems from the following relationship:

$$\eta = 7.5 \cdot \ln(H_c) + 68.2 \quad (4-1)$$

where

H_c = Henry's law constant for chemical of interest (L^3_{liq}/L^3_{gas}).

Although Equation 4-1 provides a relationship for chemical stripping efficiencies averaged over a wide range of shower operating conditions, it does provide insight into differences in potential stripping efficiencies for various types of compounds. However, application of Equation 4-1 to chemicals with Henry's law constants beyond the range of those used to develop this relationship is not recommended.

Equation 4-1 can be rearranged to solve for the value of Henry's law constant that leads to specific stripping efficiencies. For example, the value of H_c that leads to $\eta = 55\%$ is $0.19 \text{ m}^3_{liq}/\text{m}^3_{gas}$. This Henry's law constant is consistent with reported values for chloroform at 25°C

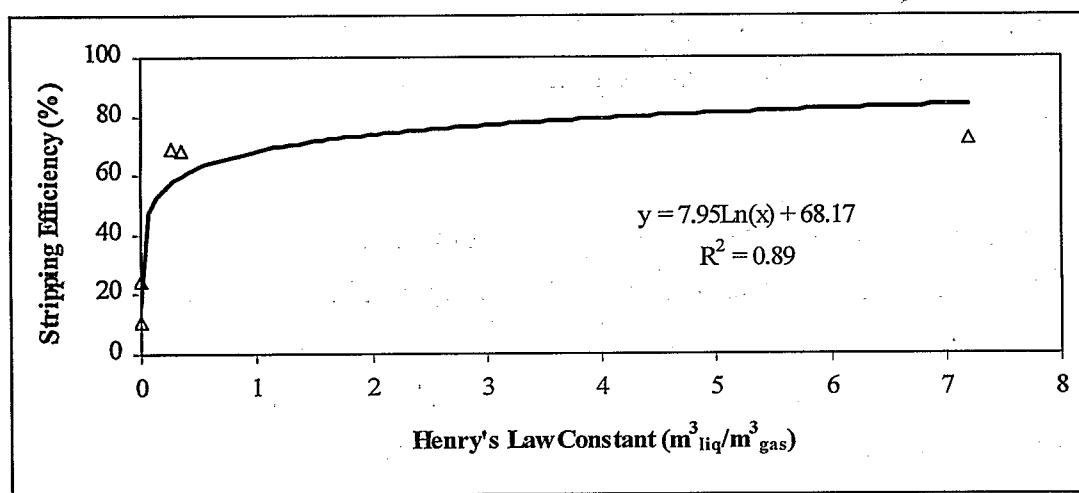


Figure 4-3. Relationship between Henry's law constant and average stripping efficiency.

(Howard, 1990), a common disinfection by-product. Tancrede et al. (1992) reported chloroform stripping efficiencies ranging from 52% to 53%, Giardino and Andelman (1991) reported a value of 55%, and Giardino and Andelman (1996) reported chloroform stripping efficiencies ranging from 44% to 52%, all in good agreement with Equation 4-1.

4.4.2. K_LA Values

Values of K_LA for each chemical tracer are reported in Tables 4-7 to 4-11. The determination of values of K_LA was based on liquid-phase data for all chemicals. Tables 4-7 through 4-11 have a format similar to that of Tables 4-2 to 4-6, except the main effects are based on values of K_LA .

Values of K_LA for acetone ranged from 1.4 to 3.7 L/minute (see Table 4-7). The highest value corresponded to the experimental conditions of warm water, high flowrate, and fine shower spray. The largest main effect was liquid flowrate, with a value of 0.93 L/minute. In a manner similar to that for stripping efficiency results, K_LA values can be grouped according to liquid flowrate, resulting in the following average values: 2.9 L/minute for high flowrate and 2.0 L/minute for low flowrate.

Liquid temperature had the second highest main effect on K_LA values for acetone. The liquid temperature main effect was 0.83 L/minute, which indicated an increase in K_LA with increased temperature. As expected from its greater surface to volume ratio, fine shower spray was determined to increase stripping efficiencies more than did coarse spray.

Values of K_LA for the replicate experiments were also compared. For Experiments 6 and 6 replicate, the relative difference in values of K_LA was 8.5%. For Experiments 8 and 8 replicate, the relative difference in values of K_LA was 8.3%.

Measured and predicted liquid-phase and gas-phase concentrations of acetone for Experiment 7 are presented in Figure 4-4, and are representative of other experiments. The operating conditions used in Experiment 7 were warm water, low flowrate, and coarse shower spray. As described in Section 4.3.3, each shower experiment was divided into three separate

Table 4-7. Acetone K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect ^a (L/min)	Liquid flowrate effect ^b (L/min)	Liquid temperature effect ^c (L/min)
1	Cold	High	Coarse	1.8	-1.2	0.40	1.0
2	Cold	High	Fine	3.0	-1.2	1.5	0.60
3	Cold	Low	Coarse	1.4	-0.10	0.40	0.80
4	Cold	Low	Fine	1.5	-0.10	1.5	0.90
5	Warm	High	Coarse	2.8	-0.80	0.60	1.0
6	Warm	High	Fine	3.4	-0.80	1.2	0.6
6 replicate	Warm	High	Fine	3.7			
7	Warm	Low	Coarse	2.2	-0.20	0.60	0.80
8	Warm	Low	Fine	2.3	-0.20	1.2	0.9
8 replicate	Warm	Low	Fine	2.5			
				Average =	-0.58	0.93	0.83

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-8. Ethyl acetate K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect ^a (L/min)	Liquid flowrate effect ^b (L/min)	Liquid temperature effect ^c (L/min)
1	Cold	High	Coarse	2.9	-1.1	0.60	2.6
2	Cold	High	Fine	4.0	-1.1	1.5	2.8
3	Cold	Low	Coarse	2.3	-0.20	0.60	1.5
4	Cold	Low	Fine	2.5	-0.20	1.5	2.5
5	Warm	High	Coarse	5.5	-1.3	1.7	2.6
6	Warm	High	Fine	6.9	-1.3	1.8	2.8
6 replicate	Warm	High	Fine	6.7			
7	Warm	Low	Coarse	3.8	-1.2	1.7	1.5
8	Warm	Low	Fine	4.7	-1.2	1.8	2.5
8 replicate	Warm	Low	Fine	5.3			
				Average =	-0.95	1.4	2.4

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-9. Toluene K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect ^a (L/min)	Liquid flowrate effect ^b (L/min)	Liquid temperature effect ^c (L/min)
1	Cold	High	Coarse	8.8	-2.2	2.6	2.2
2	Cold	High	Fine	11	-2.2	4.6	2.0
3	Cold	Low	Coarse	6.2	-0.20	2.6	2.2
4	Cold	Low	Fine	6.4	-0.20	4.6	2.2
5	Warm	High	Coarse	11	-2.0	2.6	2.2
6	Warm	High	Fine	13	-2.0	4.3	2
6 replicate	Warm	High	Fine	12			
7	Warm	Low	Coarse	8.4	-0.30	2.6	2.2
8	Warm	Low	Fine	8.1	-0.30	4.3	2.2
8 replicate	Warm	Low	Fine	9.2			
				Average =	-1.2	3.5	2.2

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-10. Ethylbenzene K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect ^a (L/min)	Liquid flowrate effect ^b (L/min)	Liquid temperature effect ^c (L/min)
1	Cold	High	Coarse	8.9	-2.1	2.9	1.1
2	Cold	High	Fine	11	-2.1	4.8	2.0
3	Cold	Low	Coarse	6.0	-0.20	2.9	2.2
4	Cold	Low	Fine	6.2	-0.20	4.8	2.2
5	Warm	High	Coarse	11	-2.0	2.8	1.1
6	Warm	High	Fine	13	-2.0	4.6	2
6 replicate	Warm	High	Fine	12			
7	Warm	Low	Coarse	8.2	-0.20	2.8	2.2
8	Warm	Low	Fine	7.9	-0.20	4.6	2.2
8 replicate	Warm	Low	Fine	8.8			
				Average =	-1.1	3.8	2.1

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

Table 4-11. Cyclohexane K_LA values for experimental shower

Experiment #	Liquid temp.	Liquid flowrate	Shower spray	K_LA (L/min)	Shower spray effect ^a (L/min)	Liquid flowrate effect ^b (L/min)	Liquid temperature effect ^c (L/min)
1	Cold	High	Coarse	9.6	-2.4	3.1	3.4
2	Cold	High	Fine	12	-2.4	5.3	2.0
3	Cold	Low	Coarse	6.5	-0.20	3.1	2.1
4	Cold	Low	Fine	6.7	-0.20	5.3	2.5
5	Warm	High	Coarse	13	-1.0	4.4	3.4
6	Warm	High	Fine	14	-1.0	4.8	2.1
6 replicate	Warm	High	Fine	13			
7	Warm	Low	Coarse	8.6	-0.60	4.4	2.0
8	Warm	Low	Fine	8.4	-0.60	4.8	2.5
8 replicate	Warm	Low	Fine	9.9			
				Average =	-1.1	4.4	2.5

^a Shower spray effect from fine to coarse.

^b Liquid flowrate effect from low to high.

^c Liquid temperature effect from cold to warm.

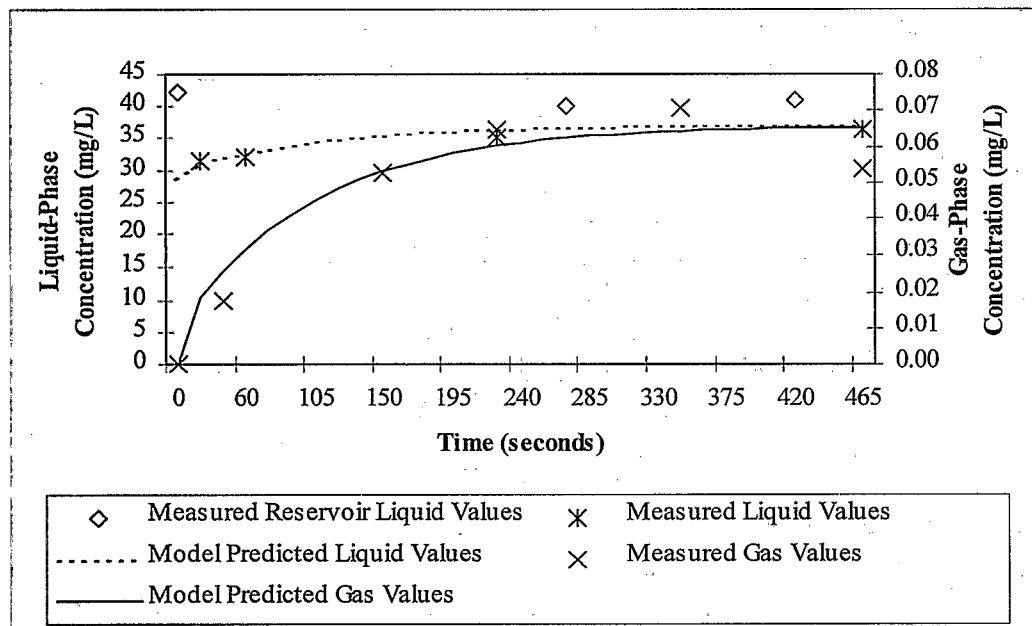


Figure 4-4. Acetone experimental data for Experiment 7.

periods: initial, intermediate, and final. As shown in Figure 4-4, each experimental period consisted of a liquid sample collected from the tracer reservoir, an outlet liquid sample, and a gas sample. For each period, the shower outlet concentration in both the liquid and gas phases may be estimated using the shower mass balance models (Equations 2-28 and 2-30). To determine the best value of $K_L A$ for the shower model, the residuals between the measured and predicted concentrations were minimized using the method described in Section 3.6.2. Two liquid samples were collected in the initial period for one gas sample. Thus, for this period the liquid-phase residual was based on the average of two measured liquid samples and a model-predicted value. For Experiment 7 shown in Figure 4-4, the best-fit value of $K_L A$ for acetone was 2.2 L/minute.

During each experiment, the chemical concentration in the tracer reservoir was relatively constant between each period. For acetone, the liquid-phase concentration measured in the shower drain tended to increase with experimental time, as mass accumulated in the shower atmosphere (gas phase). This accumulation resulted in a decreased chemical concentration driving force. The acetone gas-phase concentration continually increased during each experiment.

Values of $K_L A$ for ethyl acetate ranged from 2.3 to 6.9 L/minute, approximately 1.6 times greater than values reported for acetone. The highest value was for the experimental conditions of warm water, high flowrate, and fine spray. The largest main effect was liquid temperature, with a value of 2.4 L/minute. The average cold water value of $K_L A$ for ethyl acetate was 2.9 L/minute, and the average warm water value of $K_L A$ was 5.5 L/minute. Again, values of $K_L A$ tended to increase with increasing flowrate and fine spray.

Replicate values of $K_L A$ for ethyl acetate had a relative difference of 2.9% for Experiments 6 and 6 replicate, and 12% for Experiments 8 and 8 replicate.

Experimental results for ethyl acetate during shower Experiment 7 are presented in Figure 4-5. The value of $K_L A$ of 3.8 L/minute for this experiment was determined by minimizing the residuals between the measured liquid concentration data points and predicted liquid concentrations. As shown in Figure 4-5, for relatively constant inlet liquid concentrations (measured tracer reservoir liquid values), the measured outlet liquid-phase concentrations

increased with time. This increase in concentration reflected the decreasing chemical driving force as mass accumulated in the shower stall. As with acetone, ethyl acetate gas-phase concentrations increased with experimental time, rapidly within the first 150 seconds and more gradually thereafter. All gas-phase data in experimental plots represent measurements taken at gas sample port #1.

Values of $K_L A$ for toluene ranged from 6.2 to 13 L/minute (see Table 4-9). Similar to acetone and ethyl acetate, the operating conditions of warm water, high liquid flowrate, and fine shower spray resulted in the highest value. However, for toluene the highest main effect was not for water temperature, but rather liquid flowrate. This trend is consistent with a shift from gas-phase resistance dominating volatilization of acetone and ethyl acetate to liquid-phase resistance dominating for toluene, ethylbenzene, and cyclohexane. Because water temperature has its greatest influence on Henry's law constant, for higher values of H_c the effect of temperature is significantly reduced as the C_g/H_c term on the right-hand side of Equation 2.27 is reduced. Consequently, hydrodynamic effects on k_l and A become more important.

A main effect value of 3.5 L/minute indicated that toluene $K_L A$ values increased with

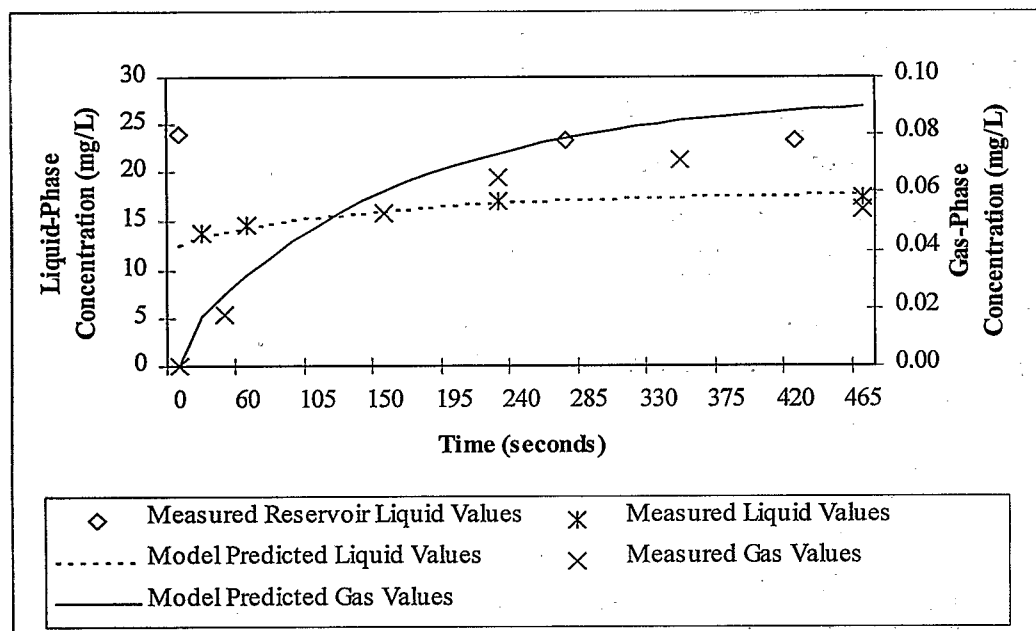


Figure 4-5. Ethyl acetate experimental data for Experiment 7.

increasing liquid flowrate. Values of $K_L A$ for toluene were grouped according to high and low flowrate, and the following average values were calculated: 11 L/minute for high flowrate experiments (Experiments 1, 2, 5, 6, and 6 replicate) and 7.7 L/minute for low flowrate experiments (Experiments 3, 4, 7, 8, and 8 replicate).

The second largest main effect was for liquid temperature, with a value of 2.2 L/minute. When the experiments were regrouped using liquid flowrate and liquid temperature, the following averages resulted: 9.9 L/minute for cold water and high flowrate (Experiments 1 and 2), 6.3 L/minute for cold water and low flowrate (Experiments 3 and 4), 12 L/minute for warm water and high flowrate (Experiments 5, 6, and 6 replicate), and 8.6 L/minute for warm water and low flowrate (Experiments 7, 8, and 8 replicate). Fine shower spray resulted in higher values of $K_L A$ for toluene than coarse spray as a result of the increased total surface area for the liquid phase.

Toluene results for Experiment 7 are presented in Figure 4-6. Differences between toluene concentrations in the tracer reservoir concentrations and shower outlet were significantly greater than differences shown in Figures 4-4 and 4-5 for acetone and ethyl acetate, respectively. This larger difference reflects the greater chemical volatilization rate for toluene, which is less affected

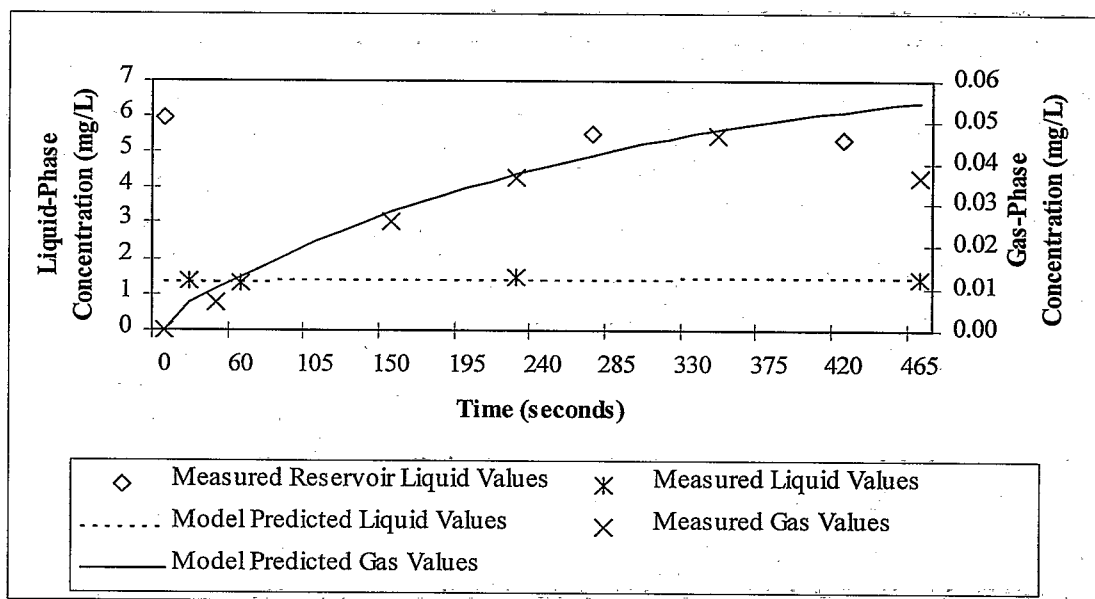


Figure 4-6. Toluene experimental data for Experiment 7.

by an approach to chemical equilibrium, that is, reduction in the concentration driving force between water and air, and gas-phase resistance to mass transfer. For toluene, the ratio of gas concentration to Henry's law constant was always small relative to inlet or outlet water concentration ($C_g/H_c \ll C_l$ in Equation 2.27). This condition led to nearly constant values of toluene concentration in water draining from the shower and constant stripping efficiencies during the course of an experiment, trends that were also observed for ethylbenzene and cyclohexane.

Values of $K_L A$ for ethylbenzene ranged from 6.0 to 13 L/minute (see Table 4-10). As expected, this range is similar in magnitude to that of toluene. Ethylbenzene also shared main effects similar to those calculated for toluene. Grouping ethylbenzene $K_L A$ values by high and low flowrate resulted in the following average values: 11 L/minute and 7.4 L/minute, respectively.

Values of $K_L A$ for ethylbenzene may also be grouped according to liquid flowrate and liquid temperature. Average values were 10 L/minute for high flowrate and cold water, 6.1 L/minute for low flowrate and cold water, 12 L/minute for high flowrate and warm water, and 8.3 L/minute for low flowrate and warm water.

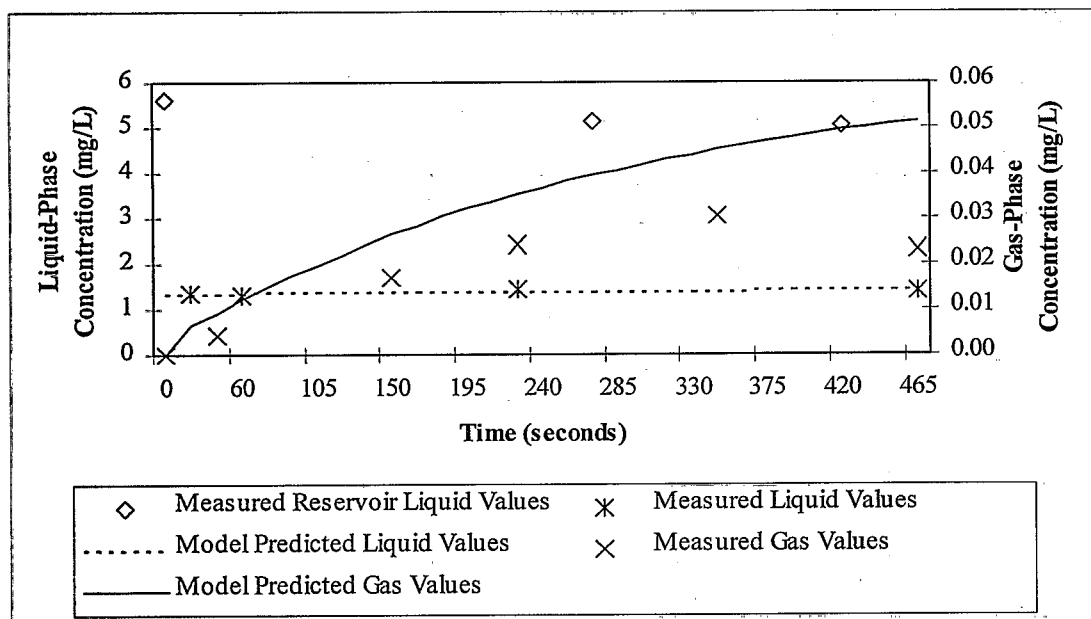


Figure 4-7. Ethylbenzene experimental data for Experiment 7.

Ethylbenzene data for Experiment 7 are plotted in Figure 4-7. Chemical concentration values and trends follow those discussed for toluene. Both chemicals had a value of $K_L A$ of 13 L/minute for this experiment.

Finally, values of $K_L A$ for cyclohexane ranged from 6.5 to 14 L/minute (see Table 4-11). The fact that cyclohexane has a significantly higher Henry's law constant than either toluene or ethylbenzene but its values of $K_L A$ were only slightly higher suggests that gas-phase resistance to mass transfer was small for each of these three tracers. Following the trend of toluene and ethylbenzene, cyclohexane also had the highest main effect value associated with liquid flowrate, with a value of 4.4 L/minute. Average values of $K_L A$ based on liquid flowrate were 12 L/minute for high flowrate and 8.0 L/minute for low flowrate.

Cyclohexane data are plotted in Figure 4-8 for Experiment 7. Again, for relatively constant inlet liquid concentrations, the outlet liquid-phase concentrations were consistent with one another. Cyclohexane gas-phase concentrations increased at a consistent rate throughout each experiment.

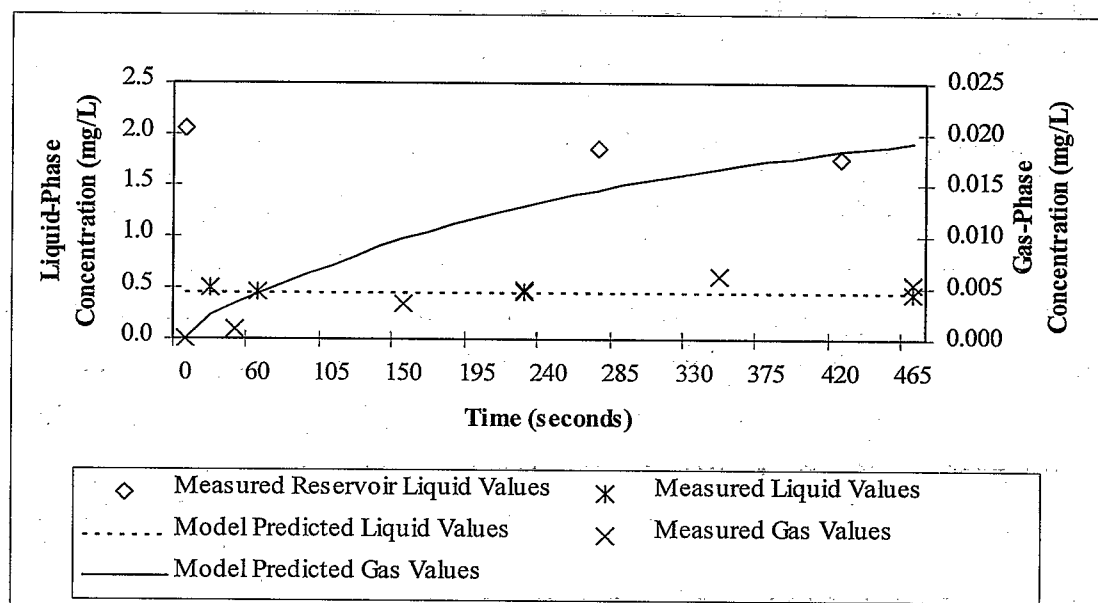


Figure 4-8. Cyclohexane experimental data for Experiment 7.

To calculate $K_L A$ for each chemical tracer using the shower mass balance models (Equations 2-28 and 2-30), the gas phase was assumed to simulate a well-mixed reactor. To check the validity of this assumption, gas-phase samples were collected at three locations within the shower atmosphere as shown in Figure 4-1. Based on the percent difference between measured gas-phase concentrations at each sample port, the shower stall appeared to be relatively well mixed. The average of percent differences (absolute values) between gas-phase samples for acetone were 18% when comparing sample port #1 and sample port #2, 16% when comparing sample port #2 and sample port #3, and 16% when comparing sample port #1 and sample port #3. The concentration differences between sample ports appeared to be random between experiments; that is, the relative differences were both positive and negative. In addition, 85% of compared samples were within 0.02 mg/L. The average percent differences for ethyl acetate were 20% when comparing sample ports #1 and #2, 17% when comparing sample ports #2 and #3, and 20% when comparing sample ports #1 and #3. The average percent differences for the remaining compounds ranged from 18% to 30%. Over 93% of the compared gas-phase samples for toluene and ethylbenzene were within 0.02 mg/L, and over 88% of the compared gas-phase samples for cyclohexane were within 0.002 mg/L. Small deviations from this well mixed assumption should have no effect on experimentally determined values of $K_L A$ for toluene, ethylbenzene, and cyclohexane, in that $C_g/H_o \ll C_l$ for these chemicals.

4.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

For future model applications, it is valuable to separate $K_L A$ into liquid- and gas-phase components, that is, $k_l A$ and $k_g A$, and to predict k_g/k_l values for different operating conditions. For a specific system, values of k_g/k_l should not vary significantly between volatile chemicals (Munz and Roberts, 1989). Values of $k_l A$ and $k_g A$ for each chemical tracer are listed in Table 4-12. A single value of k_g/k_l is presented based on all chemical tracer experimental $K_L A$ values and physicochemical properties, as described in Section 3.6.3. The relative difference between replicate experiments was 15% for Experiments 6 and 6 replicate and 3.6% for Experiments 8 and 8 replicate.

With use of the factorial analysis described in Sections 3.7 and 4.4.1, the impact of shower operating conditions on $k_l A$ and $k_g A$ was investigated. As with $K_L A$, the most significant

operating condition affecting k_lA was liquid flowrate, except for ethyl acetate, which was most affected by temperature. The most significant factor affecting k_gA was liquid flowrate, this time for all chemicals. As expected, temperature generally had a greater relative impact on k_lA than k_gA .

As shown in Table 4-12, the ratio of k_g/k_l for showers ranged from 110 to 223, with an average value of 156. This value is consistent with the typical value of 150 reported by Mackay et al. (1979). However, Little (1992) reported three values of k_g/k_l for showers based on other researchers' work (Giardino and Andelman, 1991; Tancrede et al., 1992). These values were 13 for a liquid temperature of approximately 44°C and liquid flowrate of 5 L/minute, 22 for a liquid temperature of 42°C and a liquid flowrate of 13 L/minute, and 17 for a liquid temperature of 33°C and liquid flowrate of 14 L/minute.

An important parameter that influences the back-calculation of k_g/k_l is the Henry's law constant for each chemical. As discussed in Section 4.2.1, there is uncertainty associated with Henry's law constants for chemicals, especially at elevated temperatures. Increasing the Henry's law constant for toluene in Experiment 7 by 40% results in a 1.1% decrease in K_LA . Thus, values of K_LA for chemicals of higher volatility are less sensitive to changes in Henry's law constant. However, this is not the case for chemicals such as acetone or ethyl acetate.

Table 4-12. Liquid- and gas-phase mass transfer coefficients for shower experiments

Experiment #	Chemical	k_lA (L/min)	k_gA (L/min)	k_g/k_l
1	A	13	1,986	153
	EA	7.3	1,111	
	T	9.0	1,380	
	EB	9.1	1,395	
	C	9.6	1,468	
2	A	16	3,519	223
	EA	8.1	1,807	
	T	11	2,434	
	EB	11	2,384	
	C	12	2,652	

Table 4-12. Liquid- and gas-phase mass transfer coefficients for shower experiments (continued).

Experiment #	Chemical	$k_l A$ (L/min)	$k_g A$ (L/min)	k_g/k_l
3	A	8.6	1,723	200
	EA	5.1	1,030	
	T	6.4	1,274	
	EB	6.2	1,234	
	C	6.5	1,305	
4	A	8.8	1,720	195
	EA	5.3	1,031	
	T	6.5	1,275	
	EB	6.3	1,232	
	C	6.7	1,309	
5	A	14	1,548	111
	EA	12	1,322	
	T	11	1,223	
	EB	11	1,188	
	C	13	1,439	
6	A	16	2,095	131
	EA	14	1,852	
	T	14	1,776	
	EB	13	1,708	
	C	14	1,786	
6 replicate	A	15	2,316	153
	EA	13	1,945	
	T	13	1,930	
	EB	12	1,855	
	C	13	1,950	
7	A	11	1,169	110
	EA	8.2	901	
	T	8.6	949	
	EB	8.3	917	
	C	8.6	943	
8	A	9.6	1,380	143
	EA	9.0	1,292	
	T	8.3	1,189	
	EB	8.0	1,139	
	C	8.4	1,203	
8 replicate	A	11	1,507	138
	EA	10	1,443	
	T	9.3	1,291	
	EB	8.9	1,227	
	C	9.9	1,366	

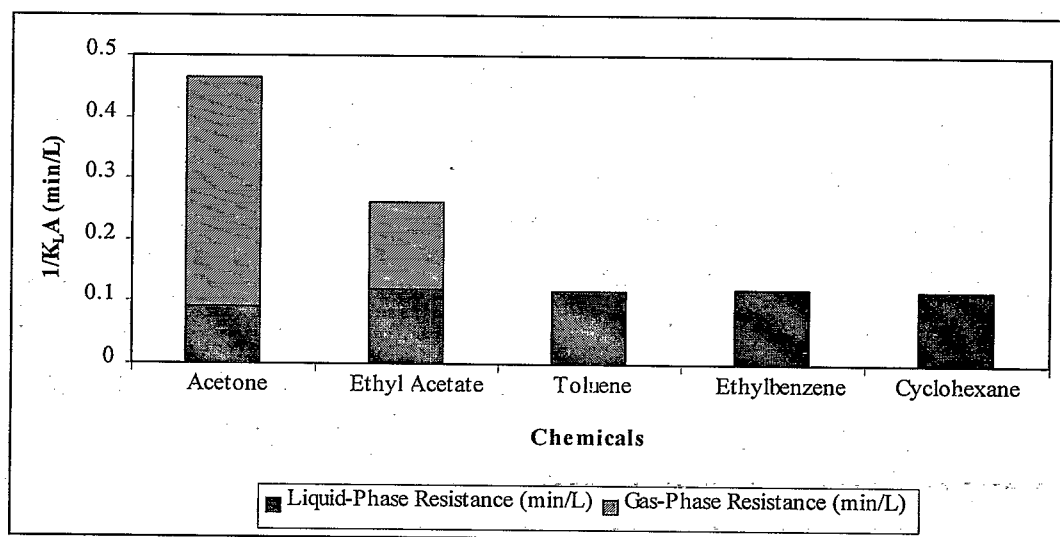


Figure 4-9. Resistances to mass transfer for each chemical in Experiment 7.

Increasing the Henry's law constants of these two chemicals by 40% results in a 17% decrease in $K_L A$ for ethyl acetate and 23% decrease in $K_L A$ for acetone. The decrease in $K_L A$ for these two compounds then results in a best-fit k_g/k_l value of 46, 58% of the value reported in Table 4-12 for Experiment 7. Interestingly, the best-fit k_g/k_l value using only toluene, ethylbenzene, and cyclohexane data from Experiment 7 was 116.

Liquid and gas-phase mass transfer coefficients may also be used to determine the relative importance of liquid and gas-phase resistances to mass transfer for specific chemicals and operating conditions. As shown in Equation 2.5, the overall resistance to mass transfer ($1/K_L A$) may be written as the sum of liquid-phase resistance to mass transfer ($1/k_l A$) and gas-phase resistance to mass transfer ($1/k_g A \cdot H_c$). These resistances are shown graphically in Figure 4-9 for each chemical in Experiment 7. As shown in Figure 4-9, the overall resistance to mass transfer for acetone is dominated by resistance in the gas phase. The overall resistance to mass transfer for ethyl acetate is distributed relatively equally between liquid-phase resistance and gas-phase resistance. Finally, the gas-phase resistances to mass transfer for toluene, ethylbenzene, and cyclohexane are insignificant relative to their respective liquid-phase resistances to mass transfer.

4.4.4. Mass Closure

For shower experiments, mass closure values as defined by Equation 3.12 ranged from 96% to 103% for acetone, 98% to 108% for ethyl acetate, 71% to 90% for toluene, 54% to 73% for ethylbenzene, and 40% to 74% for cyclohexane. The more volatile chemicals (toluene, ethylbenzene, and cyclohexane) tended to achieve mass closure values less than 100%. This may have been due to the dissolution problems described in Section 3.4.2. A separate calibration curve was developed to assess this effect, based on a 4-day standard calibration period, that is, allowing chemicals to dissolve in the Tedlar™ bag for 4 days instead of 1 day. The resulting mass closures improved for toluene (77% to 106%), ethylbenzene (64% to 92%), and cyclohexane (66% to 85%).

Previous researchers (Keating and McKone, 1993; Keating et al., 1997; Tancrede et al., 1992) have also observed differences in predicted gas-phase concentrations and measured gas-phase concentrations for volatile chemicals. It has often been suggested that there exists a second compartment in the shower system that acts as a chemical sink. Keating and McKone discussed the possibility that the second-compartment effect could be accounted for by one to all of the following: incomplete mixing within the shower stall, sorption of chemicals onto surfaces, and/or scavenging of chemicals by aerosols. A number of tests were completed to investigate these possibilities. Cyclohexane is used as the example chemical, because it had the most problems meeting the mass closure requirements.

First, a shower experiment with clean (no chemicals) warm water was completed. At the end of the experiment, sponges were used to soak up the water collected in known areas on the different types of surfaces within the shower stall (plastic-coated fiberglass wall and floor, stainless steel ceiling, and Tedlar™ shower curtain). The sponges were weighed before and after water collection to estimate total volume of water collected on each surface type. Based on this experiment, the total water volume present on surfaces at the end of an experiment was approximately 0.2 L. Using the gas-phase concentration measured for each chemical and assuming that equilibrium conditions hold at the wetted surface, the expected chemical concentration of the wall surface water may be calculated. For example, the maximum concentration measured for cyclohexane was approximately 0.01 mg/L. For a Henry's law

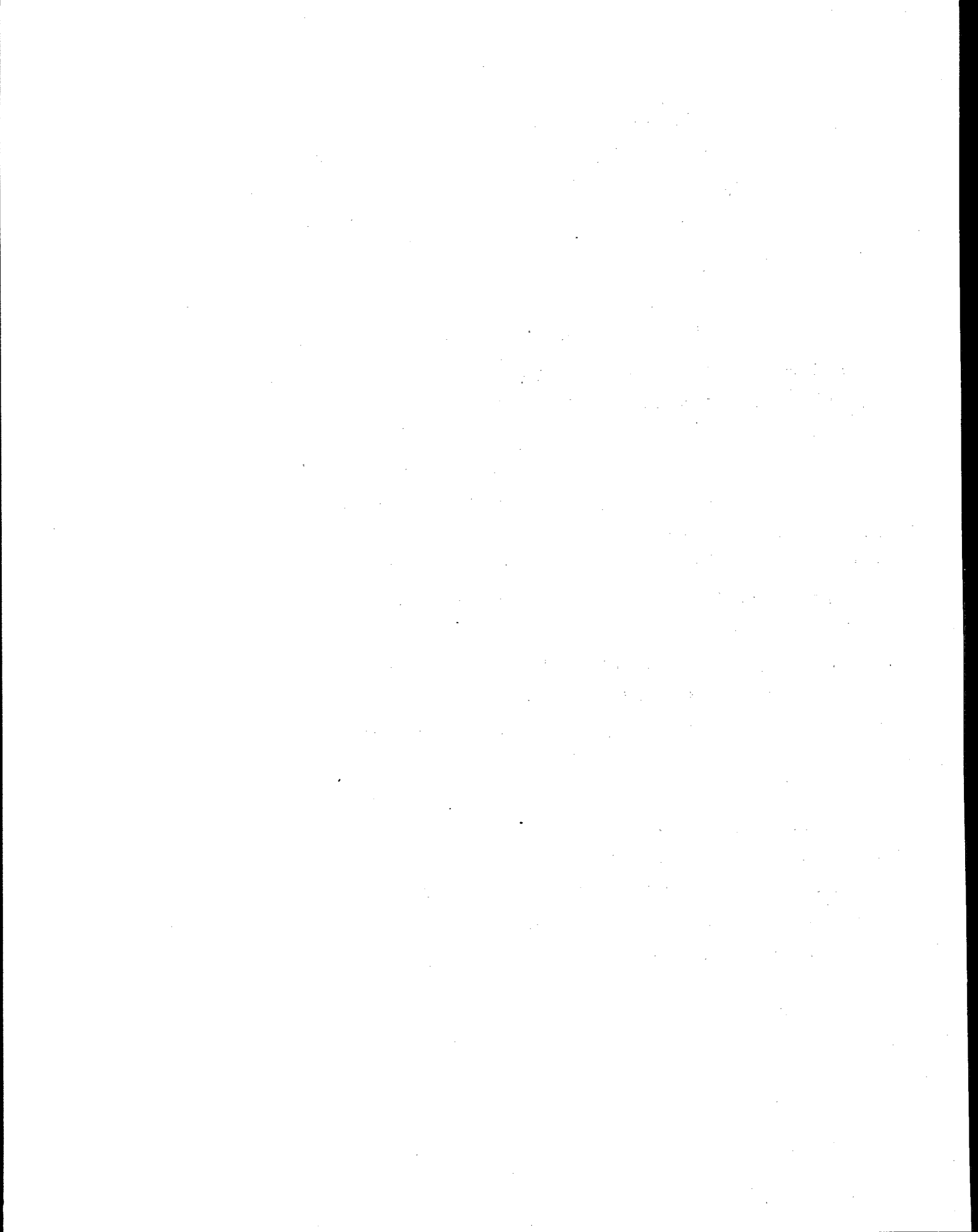
constant of $10 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$, the expected liquid-phase concentration would be 0.001 mg/L. For a total wetted surface volume of 0.2 L, the total mass to be added to the mass closure assessment would be 0.0002 mg. The total mass of cyclohexane in the shower stall gas phase was 17 mg. Therefore, the wetted surfaces were not likely to cause the difference between predicted and measured gas-phase concentrations.

As discussed in Section 4.3.1, a gas-phase sample was collected at the end of an experiment with no water flowing through the system. This sample was collected to determine the extent of chemical desorption from shower stall surfaces resulting from chemical adsorption during an experiment. Measured chemical concentrations were consistently lower than predicted values based on decay due to ventilation.

As explained in Section 4.4.2, gas-phase samples were collected at different locations within the shower stall. In general, the shower stall was determined to be well mixed. For mass closure calculations, concentrations measured at the system's exhaust port were used, and for the most part appeared to be representative of gas-phase concentrations within the shower stall.

Liquid droplet sizes produced by the experimental showerhead were not measured, making it difficult to predict the aerosol scavenging effect. On the basis of other shower studies (Keating and McKone, 1993), it is expected that this phenomenon did not contribute significantly to the chemical "sink" effect.

When possible, mass closures were determined for previously reported studies. Results were reported in the Phase I report (Corsi et al., 1996) of this project and in the Appendix to this report. In general, the mass closures determined for this study compared favorably with previously reported shower experiments and in most cases improved upon mass closures for chemicals with similar Henry's law constants.



5. DISHWASHER EXPERIMENTS

In dishwasher operation, chemicals originating in tap water can enter the machine and then be emitted to indoor air during one to five cycles (depending on wash cycle option selected). These cycles have similar operating characteristics. Thus, only a single cycle was studied experimentally. For this experimental cycle, a wide range of operating conditions was applied to adequately characterize the features associated with all of the cycles.

5.1. EXPERIMENTAL SYSTEM

A Kenmore™ dishwasher (Model No. 17651) was purchased and used for all experiments. The experimental system is illustrated in Figure 5-1. The experimental dishwasher had an interior volume of 188 L. It had five different types of wash/rinse cycle: Quick Rinse, China Light, Water Miser, Normal, and Pots and Pans. These cycle options differed only by the number of fills, that is, total volume of water used and length of operation.

The sequence of operation was as follows: the dishwasher was directly plumbed to a pressurized hot water line. At the start of each cycle, water entered the dishwasher from the hot water line at a flowrate of 4.1 L/minute. Twenty seconds after starting the fill, water from the basin pool was pumped to the rotary arm, which began spinning and spraying water throughout the dishwasher headspace. Water continued to enter the dishwasher from the hot water line for 99 seconds, such that a total of 6.8 L of water was present in the dishwasher. During the wash cycle, detergent was released from the holder as the dishwasher filled. At the end of each cycle, the water was pumped from the basin to a drain. Once all wash and rinse cycles were completed, there was an approximate 30-minute drying time.

The dishwasher was configured to allow for the required variable measurements to solve the dishwasher mass balance equations (Equations 2-23 and 2-24). A liquid sample port was installed at the bottom of the dishwasher. A 15 cm length of 0.635 cm OD Teflon™ tubing and a Teflon™ sample valve were connected to this port. The port inlet was observed to be submerged at all sampling times, and the residence time of the sample tube was estimated to be approximately 2 seconds. Liquid samples were collected as described in Section 3.3.1.

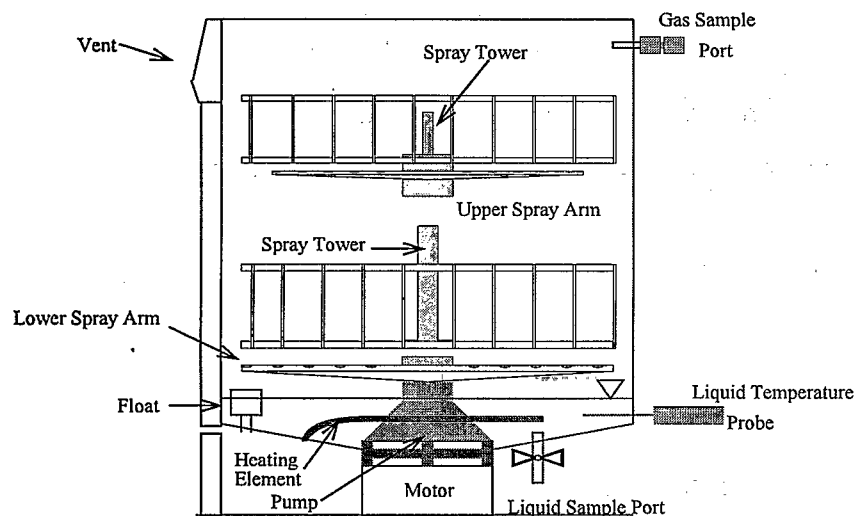


Figure 5-1. Dishwasher experimental system.

Gas samples were collected on sorbent tubes as described in Section 3.3.2. The sorbent tube was attached to a sample port located in the headspace of the dishwasher. A 2.5 cm OD Teflon™ tube was connected to the port on the inside of the dishwasher. Sample flowrates were in the range of 0.2 to 0.4 L/minute, as measured using a bubble flowmeter, and sampling times were approximately 30 seconds.

In addition to the liquid and gas sample ports, the dishwasher was configured to allow for liquid temperature monitoring. A thermocouple probe was submerged in the dishwasher pool and connected to a digital monitor to allow for constant temperature readings.

5.2. EXPERIMENTAL DESIGN

Dishwasher operating variables included water temperature, dish-loading pattern, and use of detergent (wash versus rinse portions). Experiments were designed to study the effects of these parameters on chemical volatilization rates using the $2 \times 2 \times 2$ factorial array shown in Figure 5-2. The numbers in Figure 5-2 correspond to the experiment number that was completed with the associated operating conditions. For example, Experiment 1 had the operating conditions of a rinse cycle (no detergent present), empty machine (no dishes present),

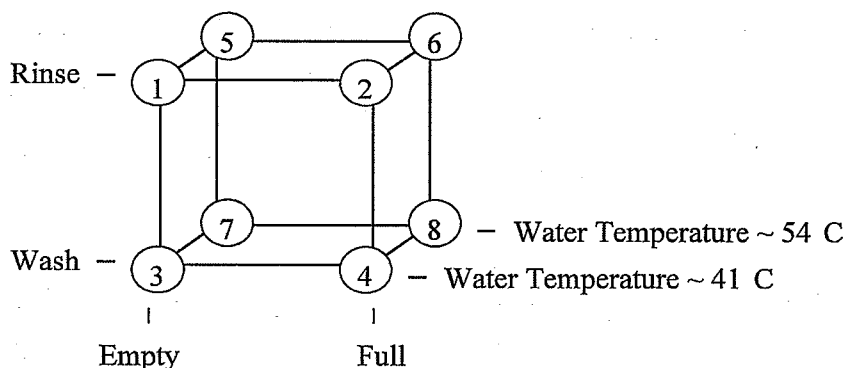


Figure 5-2. Factorial experimental design for dishwasher experiments.

and a water temperature of 41°C. In order to fulfill the factorial requirements, eight experiments were completed. Additional experiments included replicates and quality assurance tests.

5.3. SOURCE-SPECIFIC METHODOLOGY

A standard protocol was developed for preparing the dishwasher for an experiment. The following tasks were completed prior to starting an experiment:

- The appropriate dishwasher settings (normal cycle, water heat on or off) were applied
- The dishwasher was started at the beginning cycle (prerinse cycle) and allowed to run to completion of the first cycle
- The tracer bags were agitated during the first cycle
- The fill of the wash cycle (2nd cycle) was timed
- For experiments using the water heat option, the dishwasher was allowed to run until the appropriate elevated temperature (~ 54°C) was reached
- The dishwasher was stopped after fill was complete (or appropriate water temperature was reached) and the door was opened
- An initial background liquid sample was collected from the dishwasher
- The chemical tracer cocktail was added to the dishwasher basin
- The liquid-phase temperature was recorded
- An initial gas-phase sample was collected and served as the initial gas-phase concentration

- Two liquid-phase samples were collected and averaged, and served as the initial liquid-phase concentration value.

5.3.1. Sample Schedule

Experiments were designed to last 10 minutes. Experiments using the water heat option tended to be shorter, depending on cycle time required to reach the appropriate temperature. For dishwasher experiments, it was expected that a rapid loss of chemical from the liquid phase would occur in the first minute of operation, followed by a relatively constant liquid-phase concentration. The liquid-phase sample schedule was designed to reflect this behavior such that samples were collected at experimental times of 0.25, 0.75, 1.5, 3.0, and 7.0 minutes. Two additional samples were collected at 10 minutes for applicable experiments. In total, 10 liquid-phase samples were collected for each dishwasher experiment.

Gas samples were collected for 30 seconds and scheduled such that a liquid sample was collected at the midpoint of the gas sampling time. At least four gas-phase samples were collected for each experiment.

5.3.2. Ventilation Rate

A grated exhaust vent was located on the top face of the dishwasher door from which gas naturally exited the dishwasher. This ventilation rate was estimated using an isobutylene tracer gas. Isobutylene has a Henry's law constant of $23 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ and will not dissolve appreciably into dishwasher water. Before starting the dishwasher, isobutylene was introduced at 100 ppm to the dishwasher headspace. The concentration inside the dishwasher was continuously monitored using a photo-ionization detector (Photovac™ Microtip). An exponential line was fitted through data points on a plot of C_g vs. time, with the gas flowrate serving as the adjustable best-fit parameter.

5.3.3. Parameter Estimation

Experiments were completed using all five chemical tracers (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane). In addition to peaks associated with the five tracers, the GC method used to analyze liquid-phase samples (see Section 3.4.1) indicated chemical

peaks associated with compounds in the dishwasher detergent. A compound present in Cascade™ liquid dishwasher detergent eluted from the GC at the same retention time as ethyl acetate, thereby masking ethyl acetate's volatilization results. Correcting for this problem by altering the GC method resulted in a loss of definition for other tracer peaks. Thus, the original GC method was used to analyze dishwasher experimental samples, and ethyl acetate results were not reported for this source.

There were two distinct zones of chemical mass transfer for a dishwasher. Within the first 90 seconds of all experiments, a significant portion of the initial mass was volatilized to the dishwasher headspace. With the exception of cyclohexane, which completely volatilized, the dishwasher headspace behaved as if in dynamic equilibrium, a steady-state condition, for the remainder of the wash cycle (90 seconds to 10 minutes). This phenomenon made it difficult to estimate values of $K_L A$ that were representative of the entire cycle. Thus, values of $K_L A$ were determined for each chemical based on measurements collected within the first 45 seconds of an experiment. After this time the value of $K_L A$ became unimportant because the system had reached equilibrium conditions; that is, emissions could be determined via a simple equilibrium analysis without knowledge of specific mass transfer kinetics.

For cyclohexane, Equation 2-19 may be simplified to Equation 5-1 because C_g/H_c for this compound was negligible compared with C_1 for initial measured data:

$$\frac{dC_1}{dt} = -\frac{K_L A}{V_1} \cdot C_1 \quad (5-1)$$

where

- C_1 = Chemical concentration in water (M/L^3).
- t = Time (T).
- K_L = Overall mass transfer coefficient (L/T).
- A = Interfacial surface area between water and adjacent air (L^2).
- V_1 = Liquid volume (L^3).

For all experiments, cyclohexane was completely stripped from the wash water within 90 seconds. By means of measured liquid-phase concentration values from 0 to 45 seconds, a best-fit exponential curve (forced through the measured initial liquid-phase concentration value) was used to estimate $K_L A$ for cyclohexane.

Acetone, toluene, and ethylbenzene were not completely transferred from the wash water because of equilibrium limitations. As with cyclohexane, the maximum volatilization rate for the other three chemicals occurred within the first 90 seconds. At this point, however, the system was near equilibrium such that little chemical mass transferred from the liquid phase to the headspace. As for cyclohexane, an exponential curve was fitted through the first three liquid-phase concentration data points, and the negative slope of this curve multiplied by the total liquid volume resulted in a $K_L A$ value. For some experiments, this method was less accurate for toluene, ethylbenzene, and especially acetone, because of the increased C_g/H_c value as the chemicals approached equilibrium within the headspace. In those cases, the reported value of $K_L A$ would be underestimated.

Using the dishwasher mass balance models (Equations 2-23 and 2-24) also proved difficult for determining values of $K_L A$ based on the initial 45 seconds of operation because of the nature of gas sampling. First, for several experiments an initial gas-phase sample was not collected, and thus the initial gas-phase concentration was assumed to be zero. This assumption maximized the concentration driving force term in Equation 2-19, thus leading to potential underestimation of $K_L A$. Also, gas-phase samples were collected for 30 seconds, over which time the average gas-phase concentration was predicted. During the rapid volatilization period of the first minute, gas-phase concentrations for each chemical increased at an exponential rate, such that the average measured value did not accurately characterize the headspace concentration during this time. Later in the experiment, when equilibrium conditions were reached, the gas samples better represented the actual conditions.

Thus, to be consistent, the method adopted to calculate values of $K_L A$ for acetone, toluene, and ethylbenzene was the same as that used for cyclohexane. Fortunately, the exact value of $K_L A$ for these compounds is not critical because the system reached an equilibrium condition rapidly for all experiments. Knowing equilibrium will be reached, the amount of mass

transferred from the liquid phase to the gas phase can be routinely determined given knowledge of the headspace ventilation rate and Henry's law constant for a chemical of interest.

5.4. DISHWASHER RESULTS

A total of 11 dishwasher mass transfer experiments and 18 ventilation experiments were completed to characterize the emission rate from a residential dishwasher. Each mass transfer and ventilation experiment was completed with the same wash cycle. Dishwasher cycles are similar in operation, such that experimental results based on a single cycle can be applied to all cycles in order to predict total chemical emissions during use. The ventilation rates, stripping efficiencies and mass transfer coefficients ($K_L A$, $k_l A$, $k_g A$, and k_g/k_l) are presented in this chapter and are based on the experimental methodology presented in Sections 3.0 and 5.3. In addition, the effects of liquid temperature, detergent use, and dish loading pattern on each response are discussed.

The operating conditions for each mass transfer experiment are listed in Table 5-1.

5.4.1. Ventilation Rates

Ventilation rates as well as mass transfer coefficients were difficult to estimate during a single experiment. Therefore, ventilation rates were determined separately, following the

Table 5-1. Dishwasher experimental operating conditions

Experiment #	Liquid temp. (°C)	Liquid volume (L)	Headspace volume (L)	Ventilation rate (L/min)	Cycle portion type	Dish-loading pattern
1	43	7.4	181	5.7	Rinse	Empty
2	42	7.4	181	5.7	Rinse	Full
2 replicate	39	7.4	181	5.7	Rinse	Full
3	43	7.4	181	5.7	Wash	Empty
4	45	7.4	181	5.7	Wash	Full
4 replicate	38	7.4	181	5.7	Wash	Full
5	55	7.4	181	5.7	Rinse	Empty
6	55	7.4	181	5.7	Rinse	Full
7	54	7.4	181	5.7	Wash	Empty
8	55	7.4	181	5.7	Wash	Full
8 replicate	53	7.4	181	5.7	Wash	Full

methodology given in Section 5.3.2, for operating conditions similar to those used during mass transfer experiments. A total of 18 ventilation rate experiments were completed, including 11 replicate experiments. A summary of the ventilation experimental operating conditions and results is provided in Table 5-2.

As shown in Table 5-2, ventilation rates for all combinations of experimental conditions ranged from 4.6 to 7.2 L/minute. There was little deviation in ventilation rates between different water temperatures, using detergent or no detergent, and using dishes or no dishes. Thus, all experimental values were averaged to give an overall ventilation rate of 5.7 L/minute. This value was applied to all dishwasher mass transfer experimental analyses. The relatively low ventilation rate of the dishwasher allowed for low chemical emissions during operation and subsequent accumulation of chemicals in the dishwasher headspace.

A representative data plot for a ventilation experiment is shown in Figure 5-3. The experimental conditions for this plot were water heat on, detergent present, and full dishwasher (Ventilation Experiment 18). The slope for the exponential line was -0.0315 with an R^2 value of 0.99 . Values of R^2 ranged from 0.95 to 1.0 for all ventilation plots. These high R^2 values indicated a relatively constant ventilation rate for the duration of the dishwasher cycle. For this experiment, the washing machine filled at 4.1 L/minute for 99 seconds, resulting in a total liquid volume of 6.8 L. Given a total volume of 188 L, the remaining headspace volume was 181 L. The corresponding ventilation rate for this experiment was 181 L multiplied by the negative of the slope, for a value of 5.7 L/minute.

In addition to the wash cycle, ventilation rates were determined for the entire time of operation (all cycles used). In general, values based on all of the cycles did not deviate significantly from the wash cycle results. Thus, the 5.7 L/minute average ventilation rate may be applied to any dishwasher cycle.

5.4.2. Chemical Stripping Efficiencies

Chemical stripping efficiencies (η) are reported in Table 5-3 for all tracer chemicals. Stripping efficiencies for dishwasher experiments were based on the initial and final liquid-phase

Table 5-2. Dishwasher ventilation rate experimental results

Experiment #	Water heat on?	Detergent present?	Dishes present?	Ventilation rate (L/minute)	Exponential fit R^2
1	No	No	No	6.3	0.95
2	No	No	No	5.0	0.98
3	No	No	No	5	0.98
4	No	No	No	5.9	0.98
5	No	No	No	7.2	0.99
6	No	No	No	4.7	0.98
7	No	No	No	5.6	0.99
8	No	No	No	5.5	0.98
9	No	No	No	5.3	0.99
10	Yes	No	No	6.5	0.95
11	Yes	No	No	5.2	0.98
12	Yes	No	No	4.6	0.99
13	No	Yes	No	5.5	0.99
14	No	No	Yes	6.4	0.98
15	Yes	No	Yes	5.5	0.99
16	No	Yes	Yes	6.2	0.98
17	Yes	Yes	Yes	7.2	1.0
18	Yes	Yes	Yes	5.7	0.99

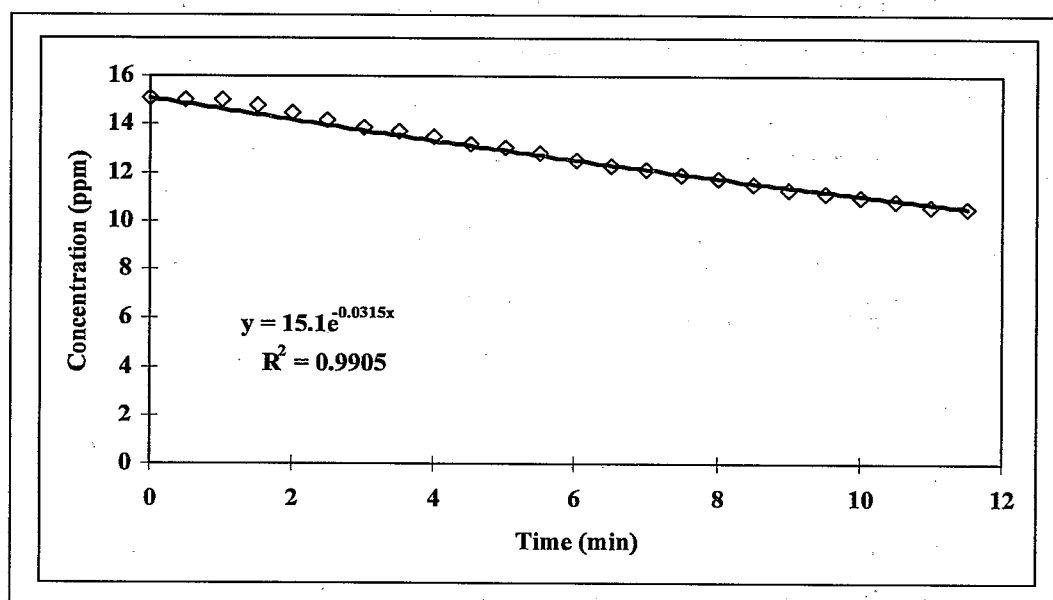


Figure 5-3. Isobutylene decay because of ventilation for Experiment 18.

Table 5-3. Chemical stripping efficiencies (η) for experimental dishwasher

Experiment #	Liquid temperature (°C)	Cycle type	Dish-loading pattern	Acetone η (%)	Toluene η (%)	Ethylbenzene η (%)	Cyclohexane η (%)
1	43	Rinse	Empty	50 ^a	97 ^a	97 ^a	100 ^a
2	42	Rinse	Full	34	96	97	100
2 replicate	39	Rinse	Full	45	97	98	100
3	43	Wash	Empty	37	96	97	100 ^a
4	45	Wash	Full	47	97	98	100
4 replicate	38	Wash	Full	42	96	97	100 ^a
5	55	Rinse	Empty	55 ^a	98	98	100
6	55	Rinse	Full	18	96	97	100 ^a
7	54	Wash	Empty	51	98	98	100
8	55	Wash	Full	37	97	97	100
8 replicate	53	Wash	Full	40 ^a	97 ^a	98 ^a	100 ^a

^aInitial liquid-phase concentration based on average of duplicate samples with a relative difference greater than 20%, but no more than 36%.

concentrations measured in the basin (Equation 2-2). The time for experiments using the water heat option was typically 3 minutes shorter than the time for experiments not using this option. Because the dishwasher headspace reached equilibrium within 2 minutes of operation, additional chemical volatilization from 7 to 10 minutes was assumed to be minimal. Thus, differences in experimental times were not accounted for in stripping efficiency results.

Stripping efficiencies for acetone ranged from 18% to 55%, with an overall average value of 41%. The highest value corresponded to the conditions of a rinse cycle, no dishes, and water temperature of 55°C.

For acetone, the stripping efficiencies were grouped to complete a factorial main effect analysis (see Section 3.7 for methodology). To illustrate this analysis, the calculation of the main effect of dish-loading pattern on stripping efficiency is presented below:

Corresponding experiments:		Difference in stripping efficiencies
1 – Average (2 and 2 rep)	=	11%
3 – Average (4 and 4 rep)	=	-8.0 %
5 - 6	=	37 %
7 – Average (8 and 8 rep)	=	12%
Average	=	13 %

As shown in this example calculation, the main effect for dish-loading pattern was 13%. A positive value indicated that stripping efficiencies for acetone tended to increase with no dishes present. Acetone's stripping efficiencies were grouped according to dish-loading pattern and averaged giving values of 48% for an empty dishwasher and 37% for a full dishwasher, both values similar in magnitude to the overall average.

The second highest main effect on acetone stripping efficiency was detergent use, with a value of -2.5%. A negative effect indicated that acetone's stripping efficiencies tended to decrease for wash cycles. Finally, the main effect with water temperature was -2.0%, indicating that stripping efficiencies for acetone tended to decrease slightly with increasing temperature. In fact, as expected, stripping efficiencies increased for two of four experiments when water temperature was increased, and decreased in the other two experiments when water temperature was increased.

Dishwasher Experiments 2, 4, and 8 were replicated. Through comparison of the acetone stripping efficiencies for these three experiments, the following relative differences were calculated: 28% for Experiments 2 and 2 replicate, 11% for Experiments 4 and 4 replicate, and 7.8% for Experiments 8 and 8 replicate.

Stripping efficiencies for toluene ranged from 96% to 98%, with an average value of 97%. Similarly, stripping efficiencies for ethylbenzene ranged from 97% to 98%, also with an average value of 97%. This narrow range in stripping efficiencies did not allow for the use of a

factorial analysis, such that no trends related to operating conditions and stripping efficiencies could be identified. However, stripping efficiencies for toluene and ethylbenzene were consistently greater than acetone, which has a lower Henry's law constant.

The relative differences in toluene stripping efficiencies between replicate experiments were 1.0% for Experiments 2 and 2 replicate, 1.0% for Experiments 4 and 4 replicate, and 0% for Experiments 8 and 8 replicate. Similarly, for ethylbenzene, relative differences were 1.0% for Experiments 2 and 2 replicate, Experiments 4 and 4 replicate, and Experiments 8 and 8 replicate, respectively.

Finally, 100% of cyclohexane volatilized for every experiment. In fact, 100% volatilization of cyclohexane was achieved within the first minute of almost all experiments. At the temperatures listed in Table 5-3, cyclohexane had Henry's law constants between 11 $\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiment 4 replicate with a temperature of 38°C) and 18 $\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiments 5, 6, and 8 replicate with a temperature of 55°C). Although no operating condition impacts could be identified, chemical stripping efficiencies did consistently increase for chemicals with increasing Henry's law constant.

Because cyclohexane achieved 100% volatilization for every experiment, the relative difference for replicate experiments was consistently 0%.

The chemical stripping efficiency results suggest that, for chemicals with a Henry's law constant greater than that for toluene, there will be nearly complete removal from the water whenever a dishwasher is used. This phenomenon is significant for many gasoline constituents, trichloroethene, tetrachloroethene, and radon. For lower volatility chemicals, stripping efficiency is defined by Henry's law.

5.4.3. K_LA Values

Values of K_LA for each chemical tracer are reported in Tables 5-4 to 5-7, respectively. Different tables were used for each chemical to show the factorial main effect analysis on each

Table 5-4. Acetone K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish-loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	7	2	1.9	1.2
2	42	Rinse	Full	4.2	2	-3.1	-3.3
2 replicate	39	Rinse	Full	5.8			
3	43	Wash	Empty	5.1	-3.0	1.9	2.5
4	45	Wash	Full	6.8	-3.0	-3.1	-3.0
4 replicate	38	Wash	Full	9.4			
5	55	Rinse	Empty	8.2	6.5	0.60	1.2
6	55	Rinse	Full	1.7	6.5	-3.4	-3.3
7	54	Wash	Empty	7.6	2.5	0.6	2.5
8	55	Wash	Full	4.9	2.5	-3.4	-3.0
8 replicate	53	Wash	Full	5.2			
				Average =	2.0	-1.0	-0.65

^a Dishes effect from full to none.

^b Detergent effect from full to none.

^c Liquid temperature effect from water heat off to water heat on.

Table 5-5. Toluene K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish-loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	33	2.0	3.0	6
2	42	Rinse	Full	30	2	-3.0	2
2 replicate	39	Rinse	Full	32			
3	43	Wash	Empty	30	-4.0	3.0	8
4	45	Wash	Full	33	-4.0	-3.0	-1.0
4 replicate	38	Wash	Full	34			
5	55	Rinse	Empty	39	6.0	1	6
6	55	Rinse	Full	33	6.0	0	2
7	54	Wash	Empty	38	5.0	1	8
8	55	Wash	Full	31	5	0	-1.0
8 replicate	53	Wash	Full	35			
				Average =	2.3	0.25	-3.8

^a Dishes effect from full to none.

^b Detergent effect full to none.

^c Liquid temperature effect from water heat off to water heat on.

Table 5-6. Ethylbenzene K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish-loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	31	-3.0	-2.0	11
2	42	Rinse	Full	32	-3.0	-2.0	2
2 replicate	39	Rinse	Full	35			
3	43	Wash	Empty	33	-3.0	-2.0	8
4	45	Wash	Full	35	-3.0	-2.0	0
4 replicate	38	Wash	Full	36			
5	55	Rinse	Empty	42	6.0	1.0	11
6	55	Rinse	Full	36	6.0	0	2
7	54	Wash	Empty	41	5.0	1.0	8
8	55	Wash	Full	34	5	0	0
8 replicate	53	Wash	Full	37			
Average =					1.3	-0.80	5.3

^a Dishes effect from full to none.

^b Detergent effect from full to none.

^c Liquid temperature effect from water heat off to water heat on.

Table 5-7. Cyclohexane K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish-loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	45	-9.0	-6.0	12
2	42	Rinse	Full	49	-9	-2	2
2 replicate	39	Rinse	Full	58			
3	43	Wash	Empty	51	-5.0	-6.0	-1
4	45	Wash	Full	50	-5	-2	-5
4 replicate	38	Wash	Full	62			
5	55	Rinse	Empty	57	1.0	7.0	12
6	55	Rinse	Full	56	1.0	5.0	2
7	54	Wash	Empty	50	-1.0	7.0	-1
8	55	Wash	Full	47	-1	5	-5
8 replicate	53	Wash	Full	55			
Average =					-3.5	1.0	2

^a Dishes effect from full to none.

^b Detergent effect from full to none.

^c Liquid temperature effect from water heat off to water heat on.

combination of operating conditions (see Section 3.7 and 5.4.2 for methodology). The three factors of the dishwasher two-level factorial arrays were liquid temperature, use of detergent, and dish-loading pattern. As shown in Tables 5-4 to 5-7, the difference in experimental response was listed twice, once for each corresponding experiment. Duplicating the listing of each difference in response, however, does not affect the average value for each variable. The experimental results for Experiments 2 and 2 replicate, 4 and 4 replicate, and 8 and 8 replicate were averaged, respectively, before applying factorial analyses.

As shown in Table 5-4, values of K_LA for acetone ranged from 1.7 to 9.5 L/minute, with an overall average value of 6.0 L/minute. The highest value corresponded to the experimental conditions of a wash cycle with dishes present, and water heat option.

The largest main effect on values of K_LA for acetone was 2.0 L/minute for the presence of dishes. In a manner similar to stripping efficiency results, values of K_LA were grouped according to the presence of dishes resulting in the following average values: 7.0 L/minute for experiments using no dishes and 5.5 L/minute for experiments using dishes.

Although a value of K_LA was roughly estimated for acetone based on the first three liquid-phase data points, experimental results clearly show acetone reached an equilibrium condition within the dishwasher headspace. Figure 5-4 shows the ratios of gas-phase and liquid-phase concentrations measured during each experiment. The shaded portion of the graph shows the range of Henry's law constants for acetone calculated based on the correlation given in Section 3.2.1 for all experiments. As shown in Figure 5-4, C_g/C_l values measured at or after 90 seconds are within or above the shaded region. A possible reason that measured C_g/C_l values exceed the given range of Henry's law constants is the potential inaccuracy of the Henry's law constant for acetone at elevated temperatures. Also, experimental error in the liquid standard calibration or gas standard calibration could lead to higher predictions of C_g/C_l . Thus, results suggest that an assumption of rapid and dynamic equilibrium is valid for lower volatility chemicals, for example, many disinfection by-products. Unfortunately, Henry's law constants are lacking for many chemicals at elevated temperatures, a fact that currently hinders accurate predictions of dishwasher emissions.

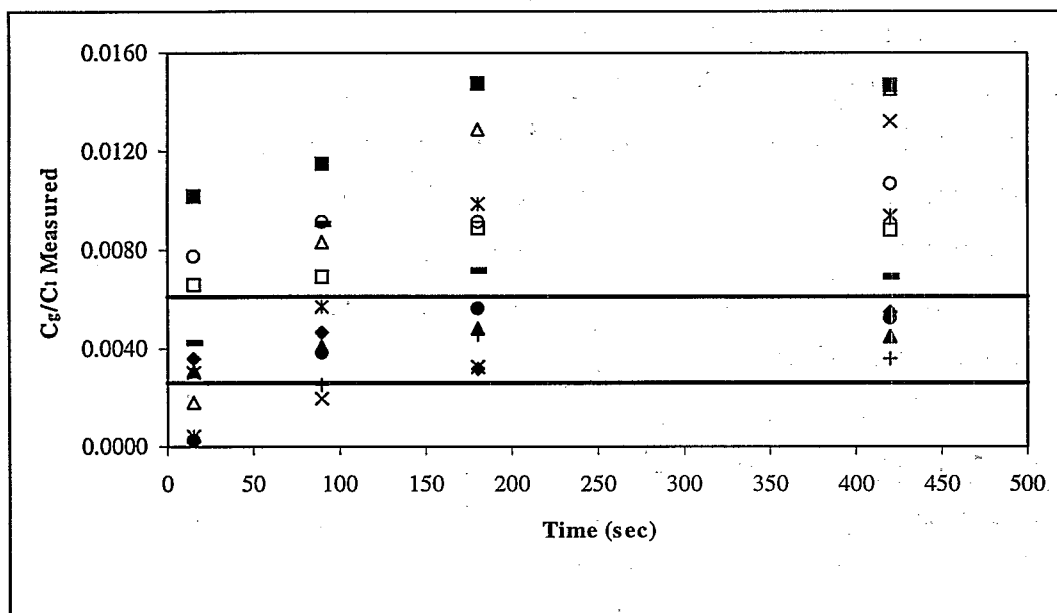


Figure 5-4. Comparison of measured C_g/C_i to predicted Henry's law constant for acetone.

Values of $K_L A$ for toluene ranged from 30 to 39 L/minute, with an overall average of 33 L/minute. Despite this relatively narrow range of values, a factorial main effect analysis was also completed for toluene. The results are presented in Table 5-5 for each set of experimental conditions. The highest main effect was for water temperature, with a value of 3.8 L/minute. Grouping values of $K_L A$ according to water temperature and averaging them gave the following results: 32 L/minute for regular hot water ($\sim 41^\circ\text{C}$) and 35 L/minute for water additionally heated by a dishwasher heating element ($\sim 54^\circ\text{C}$).

Replicate experiments had the following relative differences between values of $K_L A$ for toluene: 6.5% for Experiments 2 and 2 replicate, 3.0% for Experiments 4 and 4 replicate, and 12% for Experiments 8 and 8 replicate.

Toluene results for Experiment 8 are presented in Figure 5-5. The best-fit $K_L A$ value for this experiment was 31 L/minute. The Henry's law constant for toluene for Experiment 8 (temperature = 55°C) was $0.62 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$. Figure 5-5 illustrates the initial drop in liquid-phase concentration followed by steady-state conditions. Steady-state conditions were reached because of the dishwasher ventilation rate. In general, the ratio of C_g/C_i for measured data occurring after

100 seconds was equivalent or slightly greater than the predicted Henry's law constant for that temperature. To further illustrate this approach to equilibrium, the y-axis of Figure 5-5 is shown magnified in Figure 5-6.

Values of K_LA for ethylbenzene were slightly higher than those for toluene, with values from 31 to 42 L/minute, with an overall average of 36 L/minute. For the temperatures listed in Table 5-6, ethylbenzene had Henry's law constants ranging from $0.64 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ and $1.4 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ compared with $0.40 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ and $0.62 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ for toluene. The factorial main effects listed in Table 5-6 for ethylbenzene were also similar to those for toluene, with the highest value being 4.0 L/minute for liquid temperature. Grouping ethylbenzene K_LA values according to liquid temperature resulted in an average value of 34 L/minute for experiments with water heat off ($\sim 41^\circ\text{C}$), and 38 L/minute for water heated by dishwasher heating element ($\sim 54^\circ\text{C}$).

Replicate experiments had the following relative differences between values of K_LA for ethylbenzene: 9.0% for Experiments 2 and 2 replicate, 2.8% for Experiments 4 and 4 replicate, and 8.5% for Experiments 8 and 8 replicate.

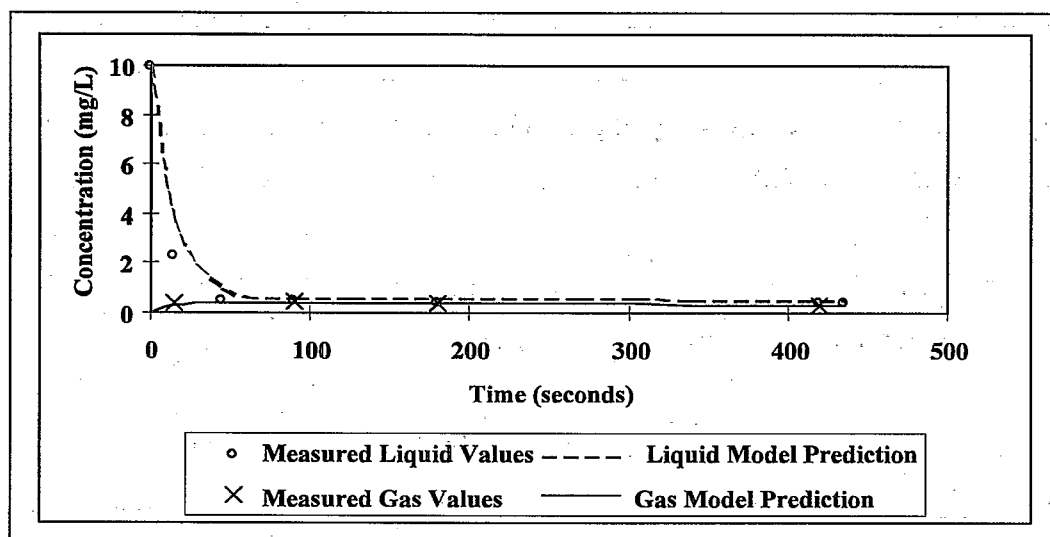


Figure 5-5. Toluene concentrations for Experiment 8.

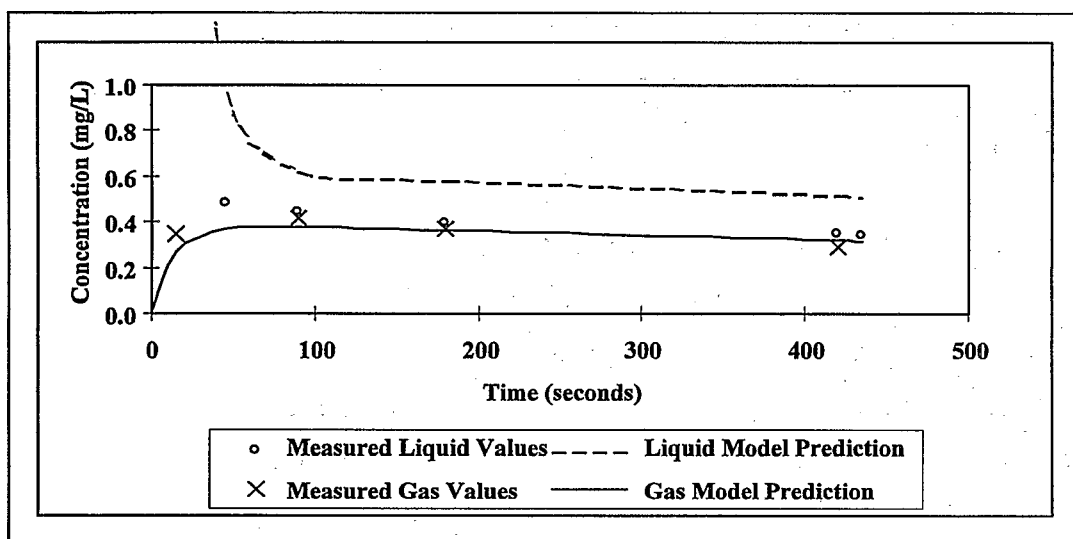


Figure 5-6. Amplification of Figure 5-5 to illustrate approach to equilibrium conditions for toluene.

Ethylbenzene results for Experiment 8 are plotted in Figure 5-7. This plot is similar to that of toluene, except the Henry's law constant for ethylbenzene at this temperature is $1.4 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$. Thus, at equilibrium, liquid-phase concentrations were less than gas-phase concentrations; that is, the gas and liquid concentration lines crossed.

Finally, values of $K_L A$ for cyclohexane ranged from 45 to 62 L/minute, with an overall average value of 53 L/minute (see Table 5-7). As expected from its relatively high Henry's law constant, cyclohexane consistently had the highest $K_L A$ value of all tracers for each experiment. Interestingly, cyclohexane had a slightly larger main effect of -3.5 L/minute associated with dish-loading pattern compared to 2.0 L/minute for liquid temperature.

Cyclohexane data for Experiment 8 are presented in Figure 5-8, which shows that cyclohexane has completely volatilized by 60 seconds into the experiment.

Replicate experiments had the following relative differences between values of $K_L A$ for cyclohexane: 17% for Experiments 2 and 2 replicate, 21% for Experiments 4 and 4 replicate, and 16% for Experiments 8 and 8 replicate.

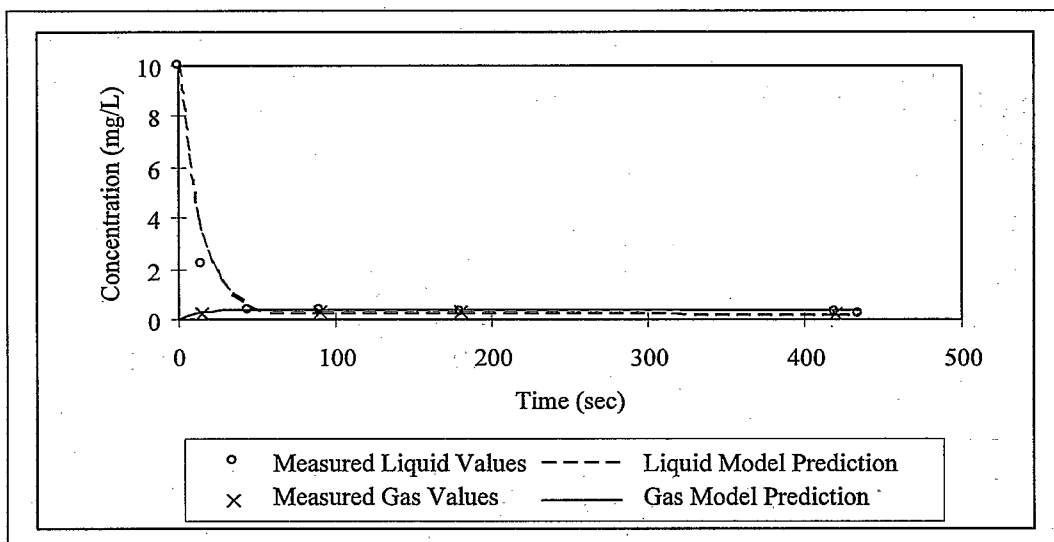


Figure 5-7. Ethylbenzene concentrations for Experiment 8.

The sensitivity of toluene's Henry's law constant on predicted emissions was also analyzed. The Henry's law constant of toluene would have to be reduced by 70% to reduce the predicted gas-phase concentrations of Experiment 8 by 10%. Thus, there is a critical value ($\approx 0.2 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$) above which the accuracy of Henry's law is not as important to the estimation of chemical emissions from dishwasher use. In this case, even though equilibrium is reached, the volume of gas is large relative to the volume of liquid such that essentially all of the chemical mass is transferred to the gas.

5.4.4. Liquid- and Gas-Phase Mass Transfer Coefficients

The extent of chemical mass transfer in a dishwasher is dictated by chemical volatility. A chemical with a relatively high Henry's law constant will completely volatilize from the dishwasher, whereas a chemical with a lower Henry's law constant will be prevented from completely volatilizing because of equilibrium limitations. For lower volatility compounds, knowledge of gas-phase resistance to mass transfer is needed only for determining the time required to reach equilibrium. For higher volatility chemicals, the time to approach complete stripping is dictated by the liquid-phase mass transfer coefficient.

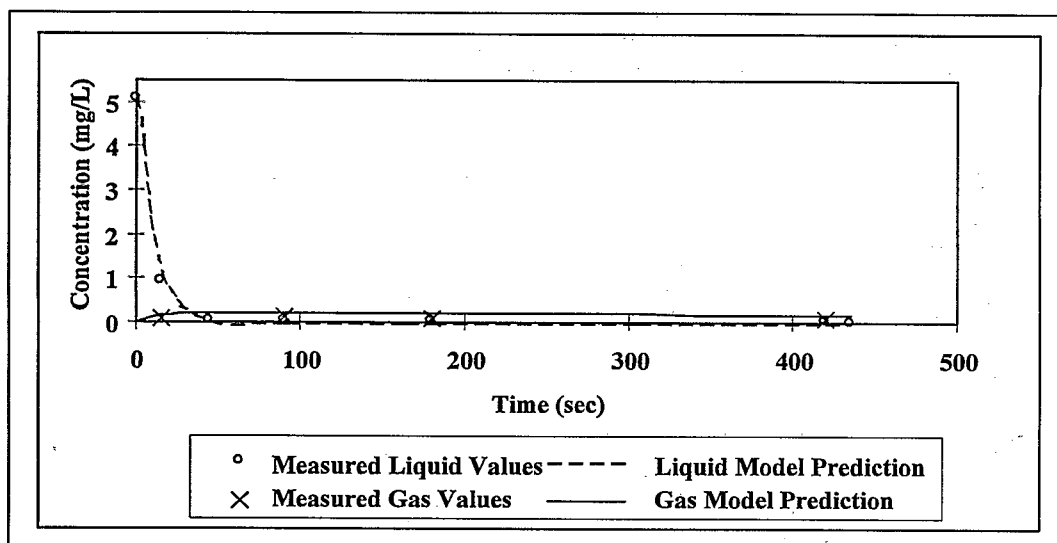


Figure 5-8. Cyclohexane concentrations for Experiment 8.

Because of the rapid approach to equilibrium for all chemicals except cyclohexane, it was not possible to determine values of $k_g A$ during dishwasher experiments. The rate of mass transfer for cyclohexane is dominated by liquid-phase resistance such that Equation 2.5 may be simplified to

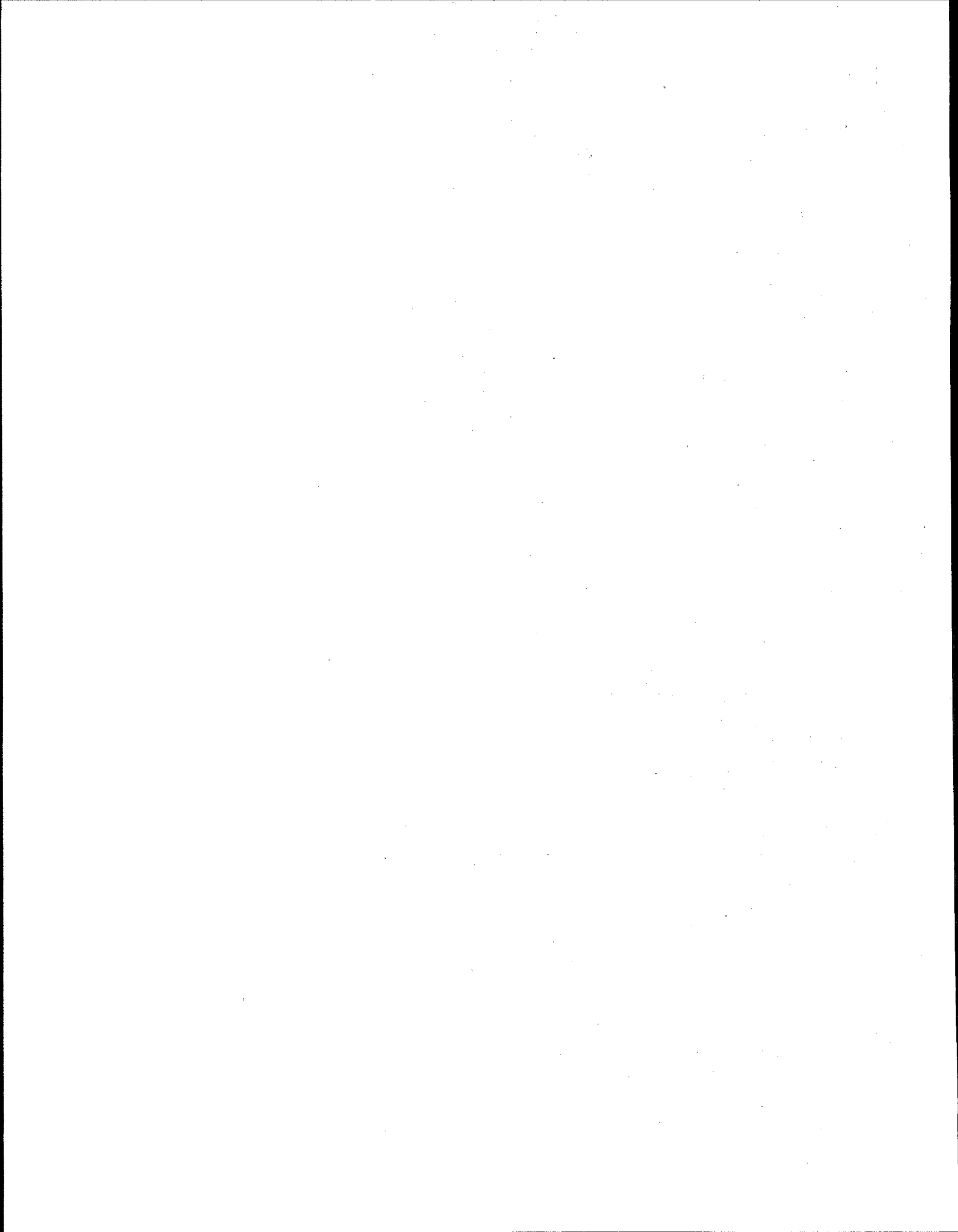
$$K_L A \cong k_L A \quad (5-2)$$

Values of $k_L A$ for any chemical of interest may be predicted using cyclohexane data and Equation 2.12. The average value of $k_L A$ for cyclohexane based on dishwasher experiments was 53 L/minute.

5.4.5. Mass Closure

An important goal for all experiments was to achieve adequate mass closure. For dishwasher experiments, mass closure was determined for separate experimental periods. An experimental period was defined when both a liquid-phase sample and a gas-phase sample were collected. Poor mixing in the initial seconds of a dishwasher experiment tended to lower the percent mass recovered for each chemical tracer in that mass closure period. Mass closure for this initial period was also difficult to assess because of gas sampling limitations. For the remaining three experimental periods, mass closure was consistent for all chemicals and was

always in the range of 84% to 124%. All mass closure values for dishwasher experiments are reported in the database in the Appendix.



6. WASHING MACHINE EXPERIMENTS

In washing machine operation, chemicals originating in a tap water supply can be emitted to indoor air during the fill and wash/rinse cycles. As previously discussed, the fill cycle is characterized by different mass transfer mechanisms from those of the wash and rinse cycles, which are similar in operation. Thus, washing machine volatilization experiments are divided into two separate groups. Fill cycle experiments are presented in Section 6.1, followed by wash/rinse cycle experiments in Section 6.2. It should be noted, however, that the results of these two experimental groups can be combined to determine an overall mass emission rate during typical washing machine operation.

6.1. FILL CYCLE EXPERIMENTS

6.1.1. Experimental System

A Kenmore™ washing machine (Model No. 25822) was purchased to complete all (both fill cycle and wash/rinse cycle) washing machine experiments. The experimental washing machine had a dual basket design with a total interior volume of 150 L (58 cm diameter and 56 cm height). Operation options included water volume setting (low, medium low, medium, medium high, high), water temperature setting (cold, warm, hot), agitation speed (slow, fast), and time of wash cycle (2 to 10 minutes).

The first action of a washing machine is to fill the tub with water. Typically, a washing machine is directly plumbed to the house water supply. However, for this project, it was necessary to add chemical tracers to the supply water upstream of the machine. To meet this need, an auxiliary water supply and pump system was added to provide inlet water to the machine (see Figure 6-1). A 120 L container served as a tracer reservoir and was filled with 60 to 90 L of tap water (depending on desired fill volume) prior to each experiment. This water was spiked with the tracer solution in a manner similar to that described in Section 3.2.2. To fill the washing machine, liquid was pumped at a prescribed flowrate from the tracer reservoir to the washing machine hose connection using a rotary vane pump (PROCON™) and 1.3 cm OD Teflon™ tubing. The liquid flowrate was confirmed by timing the collection of a known volume of liquid. An effort was made to replicate typical washing machine fill rates of 13.1 to 13.8

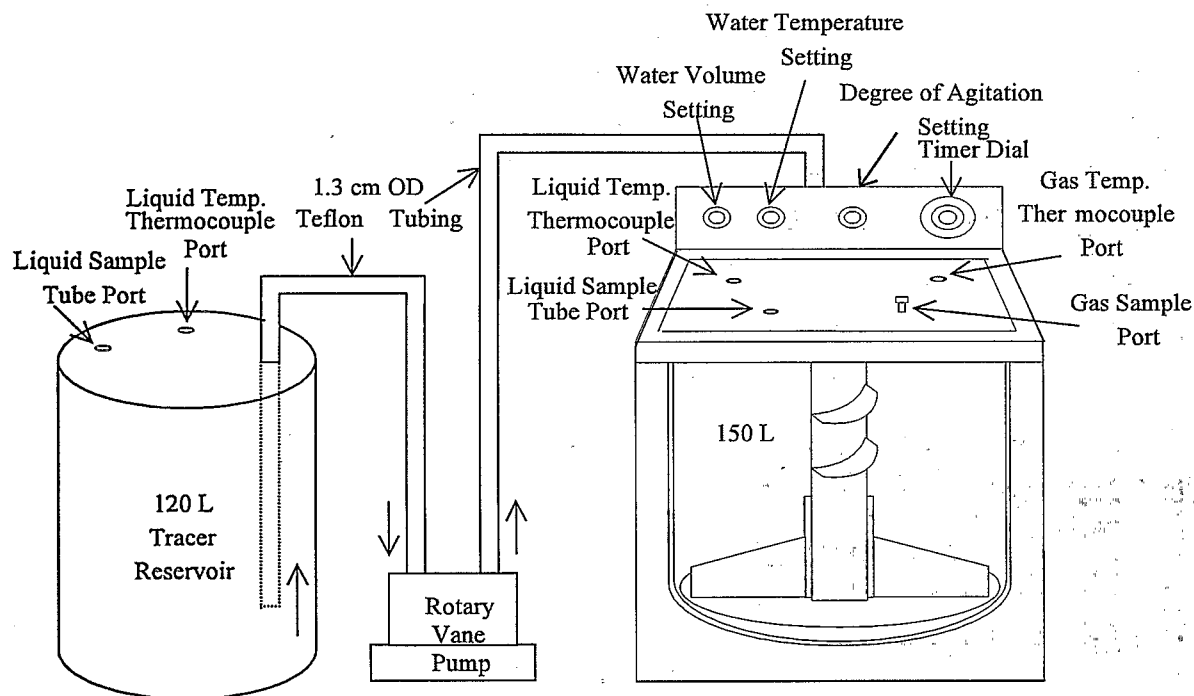


Figure 6-1. Washing machine fill cycle experimental system.

L/minute with the pump and reservoir system. In addition, typical fill times of 3 minutes and 20 seconds for low volume and 6 minutes and 25 seconds for high-volume fills were also used for appropriate experiments.

For both fill and wash/rinse cycle experiments, the washing machine was configured to allow for liquid- and gas-phase sampling. A hole 0.32 cm in diameter was drilled in the washing machine lid for liquid sampling. During an experiment, 0.32 cm OD Teflon™ tubing was inserted through the port, and liquid was pumped from the washing machine basin with a peristaltic pump (Masterflex™, L/S). After the line was flushed for 10 seconds, a liquid sample was collected in a 22 mL glass vial as described in Section 3.3.1. For fill cycle experiments, an additional liquid sample port was drilled in the tracer reservoir lid. Liquid samples from the tracer reservoir were collected in the same manner as described for the washing machine. Liquid samples collected from the tracer reservoir represented the initial liquid-phase concentration

used to solve the fill cycle mass balance equations (Equations 3-8 and 3-9), and were observed to remain relatively constant during each experiment.

For gas samples, a 0.64 cm ID bore-through stainless steel Swagelok™ fitting was inserted in the washing machine lid. A 0.64 cm OD sorbent tube was inserted through the fitting into the washing machine headspace and locked into place with a Teflon™ ferrule located inside the fitting. A gas sample was pulled through the tube as described in Section 3.3.2, at a sample flowrate between 0.2 L/minute and 0.4 L/minute. Gas sampling times for wash/rinse cycle experiments were approximately 30 seconds, whereas a single gas sample was collected for the duration of a fill cycle experiment.

Liquid-phase temperature was continuously monitored in both the tracer reservoir and the washing machine. Thermocouple wires were submerged in each basin pool and were connected to a digital monitor to allow for continuous temperature measurements. There was no significant difference in temperature between the tracer reservoir liquid and washing machine liquid for the duration of an experiment.

6.1.2. Experimental Design

Fill cycle experiments were designed to compare the volatilization rate for a standard condition with the volatilization rate associated with changes in one variable. The fill cycle standard condition was defined as cold water ($T \approx 20^{\circ}\text{C}$), no detergent, no clothes in machine, approximately 13.8 L/minute liquid flowrate, low water volume (≈ 45 L), and a fill time of 3.33 minutes. The independently varied parameters included hot water ($T \approx 50^{\circ}\text{C}$), addition of detergent (≈ 40 g of Tide™ detergent), addition of clothes (equivalent liquid volume ≈ 11 L), 8.6 L/minute liquid flowrate (4.75 minute fill time), and high water volume (≈ 90 L, 6.5 minute fill time). Six experiments and three replicates were completed.

6.1.3. Source-Specific Methodology

A standard procedure for each fill cycle was developed. Prior to the start of each experiment the following tasks were completed:

- The tracer reservoir was filled with at least 60 L of tap water (hot or cold)
- The liquid flowrate was measured and set to the appropriate value
- The tracer cocktail was added to the reservoir water and was mixed manually
- The reservoir tracer solution was mixed for an additional minute
- Detergent and/or clothes were added to the empty washing machine basin when appropriate
- Two initial liquid samples were collected from the reservoir.

It should be noted that there is no standard protocol for filling a washing machine. Users commonly add clothes and/or detergent at different times during the filling process, which incidentally results in the lid being open at different times and for varying time periods. It was not practical to replicate all possible combinations of procedures associated with loading a washing machine. Thus, a consistent protocol was adopted for all experiments. The lid was always closed, and, where applicable, clothes and/or detergent were added to the machine before the experiment was started.

6.1.3.1. *Sample Schedule*

Liquid samples were collected from the tracer reservoir throughout the experiment to monitor any chemical losses, that is, changes in the initial chemical concentrations. Five liquid samples were collected from the tracer reservoir, and four liquid samples were collected from the washing machine basin. Liquid samples from the washing machine basin were collected at experimental times of 2.0 and 2.3 minutes. Two additional samples were collected at the end of filling (3.33 minutes). These liquid sample times were adjusted for longer experiments (low flowrate and high volume). A single gas sample was collected from the washing machine headspace for the duration of the experiment, during which time sample volumes were recorded using a bubble flowmeter downstream of the adsorbent tube. A final gas sample was also collected for 30 seconds after experiment completion. Liquid temperatures were monitored for both the tracer reservoir and the washing machine.

6.1.3.2. Ventilation Rates

The experimental methodology used to estimate ventilation rates during the fill cycle was similar to that given in Section 5.3.2. However, the mass balance equation describing the washing machine headspace during filling incorporated changing liquid and headspace volumes, as shown:

$$\frac{d(C_g V_g)}{dt} = Q_g C_{g,in} - Q_g C_g \quad (6-1)$$

where

C_g = tracer gas-phase concentration in headspace (M/L^3)

V_g = headspace volume (L^3)

t = time (T)

Q_g = headspace ventilation rate (L^3/T)

$C_{g,in}$ = tracer gas-phase concentration entering headspace (M/L^3).

If one assumes the background air was relatively clean ($C_{g,in} = 0$), Equation 6-1 may be rewritten as:

$$C_g \frac{dV_g}{dt} + V_g \frac{dC_g}{dt} = -Q_g C_g \quad (6-2)$$

where

C_g = tracer gas-phase concentration in headspace (M/L^3)

V_g = headspace volume (L^3)

t = time (T)

Q_g = headspace ventilation rate (L^3/T).

Further simplifications of Equation 6.2 include rewriting the change in gas volume (dV_g/dt) as $-(dV_l)/dt$, which is equivalent to $-Q_l$. Also, the liquid volume (V_l) equals $Q_l \cdot t$. Finally, the gas volume (V_g) may be expressed as the difference between the total washing machine volume and the liquid volume ($V_t - Q_l \cdot t$). The integrated form of Equation 6-2 is then:

$$C_g = \exp \left[(Q_l - Q_g) \left(-\frac{1}{Q_l} \ln(V_t - Q_l t) + \frac{1}{(Q_l - Q_g)} \ln(C_{g,0}) + \frac{1}{Q_l} \ln(V_t) \right) \right] \quad (6-3)$$

where

C_g = tracer gas-phase concentration in headspace (M/L³)

t = time (T)

Q_g = headspace ventilation rate (L³/T).

Q_l = liquid flowrate (L³/T)

V_t = total machine volume (L³)

$C_{g,0}$ = initial tracer gas-phase concentration (M/L³).

The ventilation rate (Q_g) was determined by fitting Equation 6-3 to the measured data, using the procedure outlined in Section 3.6.

6.1.3.3. *Parameter Estimation*

Ethyl acetate was affected by the presence of detergent. As explained in Section 5.3.3, a compound present in dishwasher detergent eluted from the GC column at the same residence time as ethyl acetate, thereby masking ethyl acetate results. Interestingly, a compound present in Tide™ detergent had an opposite effect on ethyl acetate, because no peak was detected for ethyl acetate in experiments involving detergent. This result was replicated with controlled laboratory experiments in which ethyl acetate was added to vials containing water and detergent. Apparently, a detergent compound reacted with the ethyl acetate in solution such that ethyl acetate was no longer measurable using the GC/FID. Thus, ethyl acetate results are not reported for this cycle.

The duplicate liquid-phase samples collected at the end of the fill cycle were averaged to determine the $C_{l,end}$ value used in Equation 2-2 to estimate chemical stripping efficiencies. If these duplicate liquid samples were not within 20% of each other, then the average of the previous liquid samples was used to predict chemical stripping efficiency. The value of $C_{l,init}$ in Equation 2-2 was taken to be the average of liquid-phase concentrations measured in the tracer reservoir over the course of an experiment.

As discussed in Section 3.6.2, mass balance models for the fill cycle could not be solved analytically, such that a Runge-Kutta second-order numerical solution method was adopted. This method involved prediction of the following time-dependent parameters: V_l , V_g , C_l , and C_g , at 1-second intervals. The value of $K_L A$ for each chemical, except acetone, was based on minimization of the normalized residuals (Equation 3-7) between the liquid-phase concentrations measured at 2.0, 2.3, and 3.3 (experiment end time) in the washing machine basin and the model-predicted value at each of these time steps. Because the change in acetone chemical concentration in the liquid phase was relatively low, the value of $K_L A$ for acetone should be based on gas-phase data. However, for fill cycle experiments, only a single measurement was collected in the gas phase. Thus, values of $K_L A$ for acetone were based on minimizing the normalized residuals for data in both phases. The normalized residual between the final measured gas-phase concentration and the final predicted gas-phase concentration in the washing machine headspace was added to the normalized residuals between the measured liquid-phase concentrations and model predicted values.

6.1.4. Fill Cycle Results

Nine fill cycle experiments were completed to predict chemical mass emissions. Fourteen additional experiments were completed to characterize the ventilation rate during the fill cycle. Fill cycle results can be combined with wash/rinse cycle results presented in Section 6.2.4 to characterize total mass emissions during typical washing machine use. Based on the experimental methodology presented in Sections 3.0 and 6.1.3, the ventilation rates, overall chemical stripping efficiencies, and mass transfer coefficients ($K_L A$, $k_l A$, $k_g A$, and k_g/k_l) are presented in this chapter. In addition, the effects of liquid temperature, liquid volume, liquid fill rate, detergent use, presence of clothes, and chemical properties on each response are discussed.

Operating conditions for each mass transfer experiment are listed in Table 6-1. Fill cycle experiments were designed to compare a standard condition of cold water, liquid flowrate of ~13.8 L/minute, low liquid volume, no detergent or clothes in the machine, and fill time of 3.33 minutes. Experiments 1 and 1 replicate represented this standard condition. The remaining experiments have one variable that is different from the standard conditions. The differing variable is listed in the last column of Table 6-1.

Table 6-1. Washing machine fill cycle experimental conditions

Experiment #	Liquid temp. (°C)	Fill time (min:sec)	Liquid flowrate (L/min)	Liquid final volume (L)	Ventilation rate (L/min)	Headspace final volume (L)	Variable change
1	19	3:20	14.6	49	55	101	None
1 replicate	21	3:20	13.7	46	55	104	None
2	19	3:20	13.8	46	55	104	Detergent
3	21	3:20	13.7	46	55	93	Clothes
4	49	3:20	13.6	46	160	104	Hot water
4 replicate	47	3:20	13.8	46	160	104	Hot water
5	20	6:30	13.7	89	55	61	High volume
6	21	4:45	8.6	41	55	109	Low flowrate
6 replicate	19	4:45	8.5	40	55	110	Low flowrate

6.1.4.1. Ventilation Rates

Ventilation rates listed in Table 6-1 represent average values based on 14 fill cycle ventilation rates. The headspace ventilation results listed in Table 6-2 were determined as explained in Section 6.1.3.2. Several components compose the system ventilation rate. First, the process of filling involves an expanding liquid pool that naturally displaces air from the washing machine headspace. The ventilation rate is complicated because additional air is drawn into the machine by the falling film of water. Also, there are buoyancy effects at elevated temperatures.

As shown in Table 6-2, ventilation rates measured at cold temperatures were lower than at hot temperatures. Heated water had a significantly higher ventilation rate because of buoyancy (chimney) effects. Other operating variables (clothes, detergent, high volume, low flowrate) did not appear to have a significant impact on headspace ventilation. Thus, ventilation rates were averaged based on liquid temperature. The average cold water ventilation rate was 55 L/minute and the average hot water ventilation rate was 160 L/minute. These average values were applied to respective experiments using cold or hot water.

A representative plot for a ventilation experiment is shown in Figure 6-2. The experimental conditions for this plot were hot water and a liquid flowrate of 13.1 L/minute (Ventilation Experiment 13). The best-fit ventilation rate for this experiment was 157 L/minute.

Table 6-2. Washing machine fill cycle ventilation rates

Experiment #	Liquid temp. setting	Fill time (min)	Liquid flowrate (L/min)	Ventilation rate (L/min)	Variable change
1	Cold	3.0	13.8	49	None
2	Cold	3.25	13.8	33	None
3	Cold	3.25	13.8	81	None
4	Cold	3.5	13.8	33	None
5	Cold	3.5	13.8	57	None
6	Cold	2.75	13.8	42	Clothes
7	Cold	3.0	13.8	47	Detergent
8	Cold	5.5	13.8	79	High volume
9	Cold	5.5	13.8	67	High volume
10	Cold	6.0	13.8	52	High volume
11	Cold	4.75	8.6	53	Low flowrate
12	Cold	4.75	8.5	52	Low flowrate
13	Hot	2.25	13.1	157	Hot water
14	Hot	2.0	13.1	161	Hot water

6.1.4.2. Chemical Stripping Efficiencies

Chemical stripping efficiencies (η) for fill cycle experiments are reported in Table 6-3.

Stripping efficiencies for low-volume experiments (Experiments 1 to 4 replicate) were based on a fill time of 3.33 minutes. Stripping efficiencies for low fill rate experiments (Experiments 6 and 6 replicate) were based on a fill time of 4.75 minutes. Finally, chemical stripping

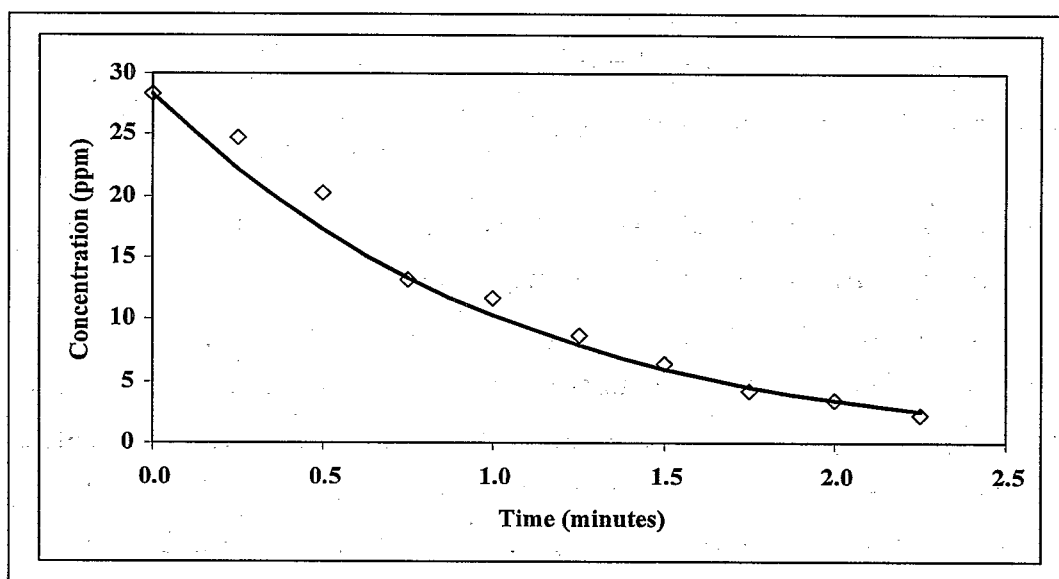


Figure 6-2. Isobutylene decay due to ventilation for Experiment 13.

Table 6-3. Chemical stripping efficiencies (η) for washing machine fill cycle

Experiment #	Variable change	Acetone η (%)	Toluene η (%)	Ethylbenzene η (%)	Cyclohexane η (%)
1	None	2.1	9.8	9.5	15
1 replicate	None	0.96	13	13	25
2	Detergent	0.74	13	16	26
3	Clothes	3.0	8.2	10	6.9
4	Hot water	1.2	22	20	28
4 replicate	Hot water	2.3	35	36	45
5	High volume	1.8	17	19	33
6	Low flowrate	1.2	23	24	37
6 replicate	Low flowrate	3.0	9.7	9.4	12

efficiencies for high-volume experiments (Experiment 5) were based on a fill time of 6.5 minutes.

The average stripping efficiencies for the standard condition (liquid flowrate \approx 13.8 L/minute, low liquid volume, no detergent or clothes in the machine, and fill time of 3.33 minutes) were 1.5% for acetone, 11% for toluene, 11% for ethylbenzene, and 20% for cyclohexane. In general, stripping efficiencies tended to increase with increasing Henry's law constant, and toluene and ethylbenzene had similar values for the same experiment. The highest stripping efficiencies for chemicals (except acetone) were associated with hot water use (average of Experiments 4 and 4 replicate). The highest stripping efficiency for acetone was for the condition of clothes in the machine (Experiment 3).

Compared with the standard case, the following conditions led to an increase in chemical stripping: detergent in the machine for toluene, ethylbenzene, and cyclohexane; clothes in the machine for acetone; and hot water and low flowrate for all chemicals. In general, however, overall stripping efficiencies were similar in magnitude for acetone. An average stripping efficiency based on all experiments was calculated to be 1.8% for acetone. For the remaining chemicals, liquid temperature appeared to be a significant factor, resulting in the following averages: 13% for cold water and 29% for hot water for toluene, 14% for cold water and 28% for hot water for ethylbenzene, and 22% for cold water and 37% for hot water for cyclohexane.

Replicate experimental results for the washing machine fill cycles were less consistent than for other sources. The reasons for high relative differences in replicate experimental results could not be determined. However, with the exception of one cyclohexane value, the absolute differences in replicate stripping efficiencies were all within 17%.

6.1.4.3. K_LA Values

As a washing machine fills, a significant quantity of air is drawn into the underlying pool. The resulting entrained air influences the rate of chemical volatilization by increasing a chemical's gas-phase resistance to mass transfer and by decreasing a chemical's concentration driving force. These factors are reflected in values of K_LA predicted for the fill cycle.

Values of K_LA for all chemicals and operating conditions are reported in Table 6-4. Values of K_LA are based on the same fill times discussed for stripping efficiencies. The average values of K_LA for the standard case were 0.23 L/minute for acetone, 2.3 L/minute for toluene, 2.3 L/minute for ethylbenzene, and 4.1 L/minute for cyclohexane. Again, there were general trends of increasing values of K_LA with increasing Henry's law constant as well as similar values for toluene and ethylbenzene. The impact of entrained air is evident from the 44% difference between ethylbenzene's K_LA and that of cyclohexane for the standard case.

As shown in Table 6-4, there was a great deal of variability in values of K_LA for acetone. Some values could not be determined by the Excel™ solver. This inconsistency likely resulted from the calculation method of K_LA and limited gas-phase data. Thus, a greater emphasis was placed on the values of K_LA for toluene, ethylbenzene, and cyclohexane for fill cycle experiments. For this particular source, the importance of gas-phase resistance to mass transfer was evident for these higher volatility compounds.

The highest values of K_LA for toluene, ethylbenzene, and cyclohexane were associated with hot water. The presence of clothes led to a reduction in values of K_LA for all chemicals. The presence of clothes in the washing machine basin visibly reduced the splashing associated with the falling liquid film and its impact in the underlying pool. In general, experiments completed with cold water resulted in similar values of K_LA . Average values of K_LA for cold water

Table 6-4. Values of $K_L A$ for washing machine fill cycles

Experiment #	Variable change	Acetone $K_L A$ (L/min)	Toluene $K_L A$ (L/min)	Ethylbenzene $K_L A$ (L/min)	Cyclohexane $K_L A$ (L/min)
1	None	0.23	1.8	1.7	2.8
1 replicate	None	n/s	2.8	2.9	5.3
2	Detergent	n/s	4.2	5.0	7.5
3	Clothes	0.086	1.5	1.9	1.2
4	Hot water	0.19	5.0	4.7	5.4
4 replicate	Hot water	0.22	8.4	8.4	11
5	High volume	0.038	2.5	2.8	4.8
6	Low flowrate	0.12	4.2	4.4	6.4
6 replicate	Low flowrate	1.2	3.5	3.7	4.5

Note: Excel solver was unable to find a feasible $K_L A$ to fit the model to the measured data.

experiments were 2.9 L/minute for toluene, 3.2 L/minute for ethylbenzene, and 4.6 L/minute for cyclohexane. For comparison, average values of $K_L A$ associated with hot water experiments were 6.7 L/minute for toluene, 6.6 L/minute for ethylbenzene, and 8.2 L/minute for cyclohexane.

6.1.4.4. Liquid and Gas-Phase Mass Transfer Coefficients

Values of $K_L A$ for each chemical were separated into the components of $k_L A$ and $k_g A$ using Equation 2-5, and a value of k_g/k_L was determined for each specific experiment. These values are reported in Table 6-5. For the fill cycle, values of k_g/k_L ranged from 4.5 to 20 with an average value of 9.5 for all experiments. A value of k_g/k_L was not determined for Experiment 3 because the Excel solver could not find a feasible solution for the available data.

Again, the variability associated with values of $K_L A$ for acetone prevented them from being incorporated into the solution matrix. Thus, values reported in Table 6-5 are based solely on toluene, ethylbenzene, and cyclohexane data. However, the last column of Table 6-5 lists the predicted average value of $K_L A$ for acetone using the reported k_g/k_L value, Equation 2-15, and experimental values of $K_L A$ for toluene, ethylbenzene, and cyclohexane. By comparison, values of $K_L A$ predicted for acetone in Table 6-5 tend to be lower than those reported for acetone in Table 6-4. However, values of $K_L A$ for acetone for Experiments 4 replicate and 5 are comparable between the predicted and measured values.

Table 6-5. Liquid and gas-phase mass transfer coefficients for washing machine fill cycle experiments

Experiment #	Chemical	$k_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_l	Predicted acetone $K_L A$ (L/min) ^a
1	T	2.9	21	7.1	0.022
	EB	2.8	20		
	C	2.9	21		
1 replicate	T	5.4	25	4.5	0.031
	EB	5.3	24		
	C	5.5	25		
2	T	7.0	47	6.7	0.056
	EB	8.1	54		
	C	7.6	51		
3	T	n/s	n/s	n/s	n/s
	EB				
	C				
4	T	5.5	111	20	0.54
	EB	4.9	101		
	C	5.4	110		
4 replicate	T	12	58	5.0	0.27
	EB	10	50		
	C	11	57		
5	T	4.6	24	5.1	0.029
	EB	5.0	26		
	C	4.9	25		
6	T	6.3	54	8.5	0.066
	EB	6.4	54		
	C	6.5	55		
6 replicate	T	4.3	80	19	0.088
	EB	4.5	84		
	C	4.5	84		

^aAcetone value of $K_L A$ based on k_g/k_l , Equation 2-15, and values of $K_L A$ for toluene, ethylbenzene, and cyclohexane.

Note: Excel solver unable to find a feasible solution.

6.1.4.5. Mass Closure

Both liquid and gas samples were collected from the filling basin such that the percentage of mass recovered could be calculated. For fill cycles, the percentage of mass recovered was based on Equation 3.11 applied for the entire time of fill. The range of mass closure for each chemical was 96% to 102% for acetone, 90% to 117% for toluene, 84% to 103% for ethylbenzene, and 69% to 102% for cyclohexane. Mass closure values for all experiments are reported in database in the Appendix.

6.2. WASH/RINSE CYCLE EXPERIMENTS

6.2.1. Experimental System

The experimental system for wash/rinse cycle experiments was similar to that shown in Figure 6-1. The same washing machine configured for liquid and gas samples described in Section 6.1.1 was used, but for wash/rinse cycle experiments it was directly plumbed to the building water supply. Chemicals were added to the washing machine basin after filling such that the auxiliary reservoir was not needed. Variable operating conditions for the wash/rinse cycle included water volume, water temperature, agitation speed, mass of clothing, and presence of detergent for a wash cycle versus none for the rinse cycle.

The wash/rinse cycle experimental system is shown in Figure 6-3. During the cycle, an impeller was used to agitate the water. The "normal" wash cycle was used for all experiments. This cycle can be varied in length. A typical value of 10 minutes was chosen for all experiments.

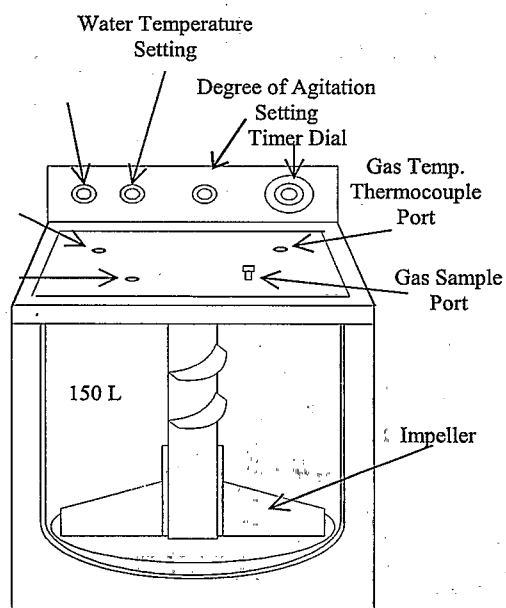


Figure 6-3. Wash/rinse cycle experimental system.

6.2.2. Experimental Design

To accommodate all of the variable operating conditions, wash and rinse cycles were studied using two ($2 \times 2 \times 2$) factorial arrays as shown in Figure 6-4. The first design consisted of a wash cycle (≈ 40 g Tide™ detergent) versus rinse cycle, hot water ($T \approx 50^\circ\text{C}$) versus cold water ($T \approx 20^\circ\text{C}$), and clothes (equivalent liquid volume ≈ 11 L) versus no clothes. The second array consisted of low water volume (≈ 45 L) versus high water volume (≈ 90 L), slow versus fast agitation speed, and cold water ($T \approx 20^\circ\text{C}$) versus hot water ($T \approx 50^\circ\text{C}$). A total of 14 experiments were completed to fulfill both factorial designs, and 3 additional experiments were completed as replicates.

6.2.3. Source-Specific Methodology

The following preexperimental tasks were completed for wash/rinse cycle experiments:

The necessary items were added to the washing machine basin (clothes and/or detergent)

The appropriate settings for a particular experiment (water volume, agitation speed, water temperature) were applied

The washing machine wash time was set to 10 minutes

The washing machine was filled with a known volume of water

The washing machine operation was stopped after the fill was complete (before agitation cycle began)

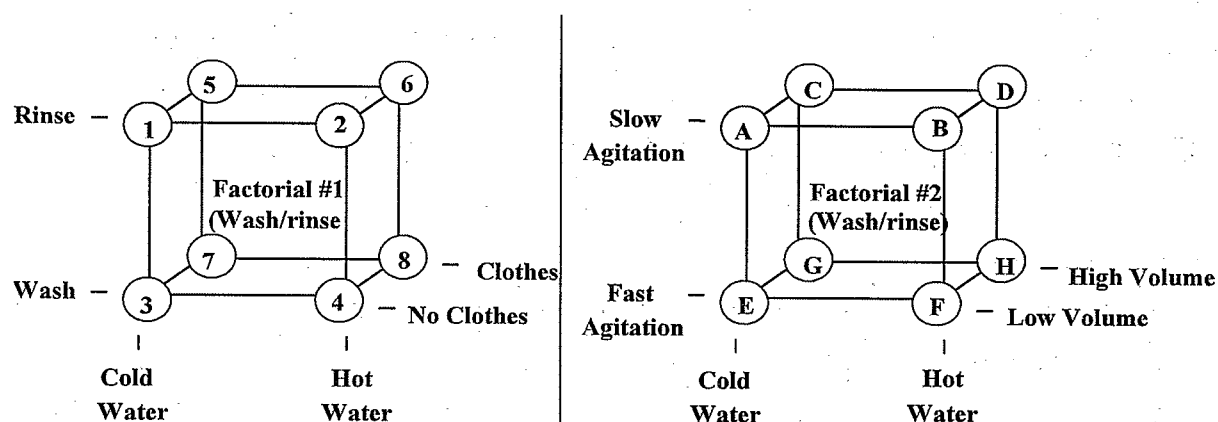


Figure 6-4. Wash/rinse cycle factorial experimental design.

- A background water sample was collected
- The chemical tracer solution was added to the washing machine basin and was mixed well (manually)
- The washing machine lid was closed
- An initial liquid sample was collected that corresponded to the initial liquid-phase concentration for an experiment
- An initial gas sample was collected that corresponded to the initial gas-phase concentration for an experiment.

6.2.3.1. Sample Schedule

A total of 12 liquid samples were collected for each wash/rinse cycle experiment. In addition to initial samples, liquid samples were collected at the experimental times of .5, 1.25, 1.75, 2.75, 3.25, 6.75, and 7.25 minutes. Two additional samples were collected at 10 minutes. These sampling times corresponded to the start and end times of each respective gas sample. For example, a gas sample was collected from time 0 to 30 seconds, 1.25 to 1.75, and so on. Including the initial sample, six gas samples were collected for each experiment. Liquid and gas-phase temperatures were recorded for the duration of the experiment.

6.2.3.2. Ventilation Rates

Washing machines are characterized by a relatively high ventilation rate. This rate was determined for all wash/rinse cycle experimental conditions using the same methodology as described in Section 5.3.2. Ventilation rates determined using isobutylene decay were used in wash/rinse cycle mass balance models with data from mass transfer experiments.

6.2.3.3. Parameter Estimation

An important measurement used to determine chemical stripping efficiencies and mass transfer coefficients was the initial liquid-phase concentration. For several experiments, the liquid-phase concentration increased in magnitude for various lengths of time before decreasing as expected. This initial increase was likely caused by improved mixing of the chemical tracer solution in the washbasin. For consistency, each chemical's stripping efficiency was calculated based on the highest measured liquid-phase concentration during an experiment and the final

measured liquid-phase concentration. This procedure resulted in experimental stripping efficiencies based on different time periods; for example, an experiment with the highest liquid-phase concentration at time zero had a total time of 10 minutes, and an experiment with the highest value occurring after 2 minutes into the experiment had a total time of only 8 minutes. To correct for this time difference, a plot was constructed based on measured liquid-phase concentration values versus time. For experiments with a late initial concentration peak, a curve was fitted to the data and extended to reach 10 minutes. On the basis of the graph's liquid-phase concentration value at 10 minutes and the measured initial concentration, a 10-minute stripping efficiency was reported for every experiment.

Values of $K_L A$ for each chemical were calculated based on measurements collected from an experimental time of 180 seconds to the end of the experiment. This method ensured that the washing machine contents were well mixed. The difference in experimental time should not affect the reported $K_L A$ values for each chemical, as long as equilibrium conditions did not exist in the machine's headspace. Values of $K_L A$ for acetone and ethyl acetate were based on minimizing the residuals between the model and gas-phase data. Values of $K_L A$ for toluene, ethylbenzene, and cyclohexane were based on minimizing the residuals between the model and liquid-phase data. For experiments with conditions leading to relatively high volatilization rates, the more volatile chemicals often had results below the predetermined method detection level (see Section 3.5.4). In these cases, the determination of $K_L A$ was modified to include only measurements meeting this quality assurance requirement, that is, above method detection limit.

6.2.4. Wash/Rinse Cycle Results

A total of 17 wash/rinse cycle mass transfer experiments and 17 ventilation experiments were completed to characterize the emission rate from a residential washing machine during these cycles. Wash and rinse cycle results can be combined with fill cycle results presented in Section 6.1.4 to characterize total mass emissions during typical washing machine use. Based on the experimental methodology presented in Sections 3.0 and 6.2.3, the ventilation rates, overall chemical stripping efficiencies and mass transfer coefficients ($K_L A$, $k_l A$, $k_g A$, and k_g/k_l) are

presented in this chapter. In addition, the effects of liquid temperature, liquid volume, detergent use, mass of clothes, agitation speed, and chemical properties on each response are discussed.

The operating conditions for each mass transfer experiment are given in Table 6-6.

6.2.4.1. Ventilation Rates

It was difficult to estimate ventilation rates and mass transfer coefficients during a single experiment. Therefore, ventilation rates were predicted separately, following the methodology given in Section 5.3.2, for similar operating conditions used during mass transfer experiments. A total of 17 ventilation rate experiments were completed including 9 replicate experiments. A summary of the ventilation experimental operating conditions and results is provided in Table 6-7.

As shown in Table 6-7, ventilation rates measured at cold temperatures were significantly lower than ventilation rates measured at hot temperatures. The heated water led to a buoyancy (chimney) effect, which acted to flush the headspace at a faster rate. Other factors such as agitation speed, mass of clothing, presence of detergent, and volume of water had less impact on

Table 6-6. Washing machine wash/rinse cycle experimental operating conditions

Experiment #	Liquid temp. (°C)	Liquid volume (L)	Headspace volume (L)	Ventilation rate (L/min)	Agitation speed	Detergent present?	Clothes present?
1, A	24	47	103	53	Slow	No	No
1, A replicate	22	49	101	53	Slow	No	No
2, B	49	48	102	200	Slow	No	No
3	23	49	101	53	Slow	Yes	No
3 replicate	22	47	103	53	Slow	Yes	No
4	51	49	101	200	Slow	Yes	No
5	21	50	88	53	Slow	No	Yes
6	50	47	92	200	Slow	No	Yes
7	18	49	90	53	Slow	Yes	Yes
8	49	49	90	200	Slow	Yes	Yes
C	21	82	58	53	Slow	No	No
C replicate	21	95	55	53	Slow	No	No
D	51	96	54	200	Slow	No	No
E	20	48	102	53	Fast	No	No
F	49	49	101	200	Fast	No	No
G	18	95	55	53	Fast	No	No
H	50	94	56	200	Fast	No	No

Table 6-7. Ventilation rate experiment results

Experiment #	Water temperature	Water volume	Agitation speed	Detergent present?	Clothes present?	Ventilation rate (L/min)
1	Cold	Low	Slow	No	No	50
2	Cold	Low	Slow	No	No	63
3	Cold	Low	Slow	No	No	43
4	Cold	High	Slow	No	No	35
5	Cold	High	Slow	No	No	38
6	Cold	Low	Fast	No	No	78
7	Cold	Low	Fast	No	No	41
8	Cold	Low	Fast	No	No	51
9	Cold	Low	Slow	Yes	No	41
10	Cold	Low	Slow	Yes	No	64
11	Cold	Low	Slow	No	Yes	77
12	Hot	Low	Slow	No	No	116
13	Hot	Low	Slow	No	No	254
14	Hot	Low	Slow	No	No	160
15	Hot	High	Slow	No	No	246
16	Hot	Low	Slow	No	Yes	184
17	Hot	Low	Slow	No	Yes	210

the wash/rinse cycle ventilation rate. To determine an appropriate ventilation rate to use in conjunction with mass transfer data, ventilation experimental values were grouped according to water temperature. The average cold water ventilation rate was assumed to be 53 L/minute and was applied to all mass transfer data analyses based on experiments using cold water. The average hot water ventilation rate was assumed to be 200 L/minute and was applied to all mass transfer data analyses based on hot water experiments.

A representative data plot for a ventilation experiment is shown in Figure 6-5. The experimental conditions for this plot were cold water, no clothes, no detergent, low water volume, and fast agitation. The slope for the exponential line was -0.492 with an R^2 value of 0.99 . Values of R^2 ranged from 0.88 to 0.997 for all ventilation plots, with all but one value above 0.93 . These high correlation values indicated a relatively constant ventilation rate for the duration of the wash/rinse cycle. For this experiment, the washing machine filled at 13.8 L/minute for 3.43 minutes, resulting in a total liquid volume of 47 L. Based on a total volume of 150 L, the remaining headspace volume was 103 L. The corresponding ventilation rate for this experiment was 103 L multiplied by the negative of the slope for a value of 51 L/minute.

6.2.4.2. Chemical Stripping Efficiencies

Chemical stripping efficiencies are reported in Tables 6-8 to 6-16 for each chemical, respectively. The results for each chemical are reported in two tables based on each factorial design. The three factors incorporated into the first group were liquid temperature, mass of

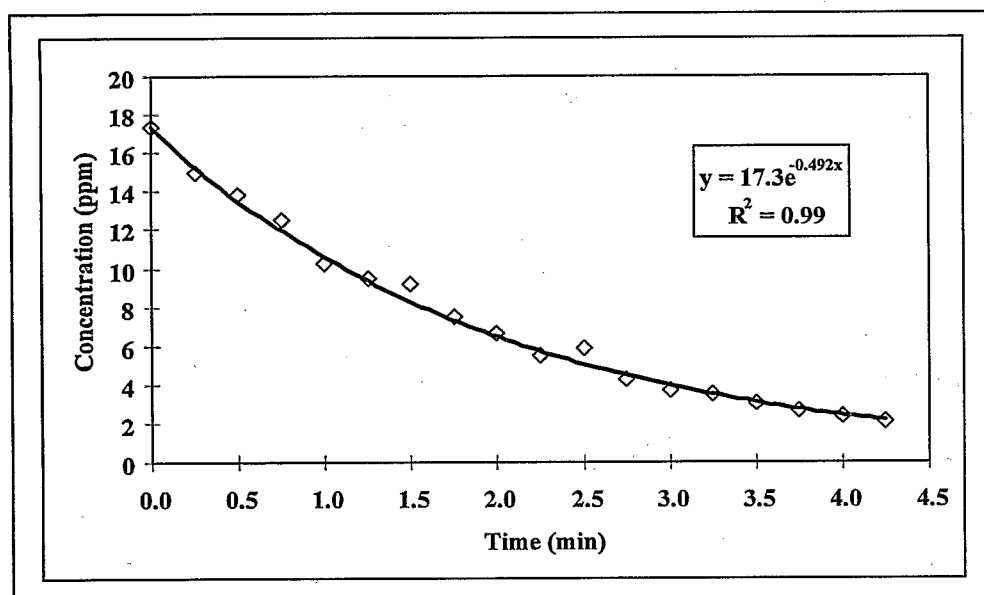


Figure 6-5. Isobutylene decay due to ventilation for Experiment 8.

Table 6-8. Acetone stripping efficiencies for washing machine wash/rinse cycle — Factorial #1

Experiment #	Liquid temp.	Detergent ?	Clothes ?	Stripping efficiency (%)	Clothes effect ^a (%)	Detergent effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	No	no	7.1	-8.0	-1.0	25
1 replicate	Cold	No	no	15			
2	Hot	No	no	36	27	6.0	25
3	Cold	Yes	no	7.0	-8.0	-1.0	18
3 replicate	Cold	Yes	no	5.1			
4	Hot	Yes	no	30	8.0	6.0	18
5	Cold	No	Yes	19	-8.0	-1.0	-9.6
6	Hot	No	Yes	9.4	27	-13	-9.6
7	Cold	Yes	Yes	20	-8.0	-1.0	2.0
8	Hot	Yes	Yes	22	8.0	-13	2.0
Average =					4.7	-2.2	8.9

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

**Table 6-9. Acetone stripping efficiencies for washing machine wash/rinse cycle—
Factorial #2**

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect ^a (%)	Liquid volume effect ^b (%)	Liquid temperature effect ^c (%)
A	Cold	Low	Slow	7.1	-5.0	6.9	25
A replicate	Cold	Low	Slow	15			
B	Hot	Low	Slow	36	5.0	33	25
C	Cold	High	Slow	3.4	-5.9	6.9	1.0
C replicate	Cold	High	Slow	4.8			
D	Hot	High	Slow	3.1	-12	33	1.0
E	Cold	Low	Fast	16	-5.0	6.0	15
F	Hot	Low	Fast	31	5.0	16	15
G	Cold	High	Fast	10	-5.9	6.0	5.0
H	Hot	High	Fast	15	-12	16	5.0
Average =					-4.5	15	11

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

**Table 6-10. Ethyl acetate stripping efficiencies for washing machine wash/rinse cycle—
Factorial #2**

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect ^a (%)	Liquid volume effect ^b (%)	Liquid temperature effect ^c (%)
A	Cold	Low	Slow	12	-6.0	4.8	38
A replicate	Cold	Low	Slow	8.1			
B	Hot	Low	Slow	48	14	43	38
C	Cold	High	Slow	5.2	-2.6	4.8	0.10
C replicate	Cold	High	Slow	5.2			
D	Hot	High	Slow	5.1	-17	43	0.10
E	Cold	Low	Fast	16	-6.0	8.2	18
F	Hot	Low	Fast	34	14	12	18
G	Cold	High	Fast	7.8	-2.6	8.2	14
H	Hot	High	Fast	22	-17	12	14
Average =					-2.9	17	18

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

**Table 6-11. Toluene stripping efficiencies for washing machine wash/rinse cycle—
Factorial #1**

Experiment #	Liquid temp.	Detergent ?	Clothes ?	Stripping efficiency (%)	Clothes effect ^a (%)	Detergent effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	No	no	72	24	35	26
1 replicate	Cold	No	no	65			
2	Hot	No	no	95	39	28	26
3	Cold	Yes	no	33	-8.0	35	33
3 replicate	Cold	Yes	no	34			
4	Hot	Yes	no	67	5.0	28	33
5	Cold	No	Yes	45	24	3.0	11
6	Hot	No	Yes	56	39	-6.0	11
7	Cold	Yes	Yes	42	-8.0	3.0	20
8	Hot	Yes	Yes	62	5.0	-6.0	20
				Average =	15	15	23

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

**Table 6-12. Toluene stripping efficiencies for washing machine wash/rinse cycle—
Factorial #2**

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect ^a (%)	Liquid volume effect ^b (%)	Liquid temperature effect ^c (%)
A	Cold	Low	Slow	72	-1.0	42	26
A replicate	Cold	Low	Slow	65			
B	Hot	Low	Slow	95	-4.0	62	26
C	Cold	High	Slow	26	3.0	42	6.0
C replicate	Cold	High	Slow	28			
D	Hot	High	Slow	33	0.0	62	6.0
E	Cold	Low	Fast	70	-1.0	46	29
F	Hot	Low	Fast	99	-4.0	66	29
G	Cold	High	Fast	24	3.0	46	9.0
H	Hot	High	Fast	33	0.0	66	9.0
				Average =	-0.50	54	18

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

**Table 6-13. Ethylbenzene stripping efficiencies for washing machine wash/rinse cycle—
Factorial #1**

Experient #	Liquid Temp.	Detergent ?	Clothes ?	Stripping efficiency (%)	Clothes effect ^a (%)	Detergent effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	No	No	76	16	36	24
1 replicate	Cold	No	No	69			
2	Hot	No	No	97	32	25	24
3	Cold	Yes	No	36	-17	36	35
3 replicate	Cold	Yes	no	37			
4	Hot	Yes	No	72	3.0	25	35
5	Cold	No	Yes	57	16	3.0	8.0
6	Hot	No	Yes	65	32	-4.0	8.0
7	Cold	Yes	Yes	54	-17	3.0	15
8	Hot	Yes	Yes	69	3.0	-4.0	15
Average =					8.5	15	21

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

**Table 6-14. Ethylbenzene stripping efficiencies for washing machine wash/rinse cycle—
Factorial #2**

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect ^a (%)	Liquid volume effect ^b (%)	Liquid temperature effect ^c (%)
A	Cold	Low	Slow	76	-1.0	43	24
A replicate	Cold	Low	Slow	69			
B	Hot	Low	Slow	97	-2.0	65	24
C	Cold	High	Slow	28	6.0	43	2.0
C replicate	Cold	High	Slow	31			
D	Hot	High	Slow	32	-2.0	65	2.0
E	Cold	Low	Fast	74	-1.0	50	25
F	Hot	Low	Fast	99	-2.0	65	25
G	Cold	High	Fast	24	6.0	50	10
H	Hot	High	Fast	34	-2.0	65	10
Average =					0.25	56	15

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

Table 6-15. Cyclohexane stripping efficiencies for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent ?	Clothes ?	Stripping efficiency (%)	Clothes effect ^a (%)	Detergent effect ^b (%)	Liquid temperature effect ^c (%)
1	Cold	No	No	99	20	20	1.0
1 replicate	Cold	No	No	99			
2	Hot	No	No	100	16	2.0	1.0
3	Cold	Yes	No	82	0.0	20	19
3 replicate	Cold	Yes	No	76			
4	Hot	Yes	No	98	4.0	2.0	19
5	Cold	No	Yes	79	20	0.0	5.0
6	Hot	No	Yes	84	16	-10	5.0
7	Cold	Yes	Yes	79	0.0	0.0	15
8	Hot	Yes	Yes	94	4.0	-10	15
Average =					10	3.0	10

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

Table 6-16. Cyclohexane stripping efficiencies for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	Stripping efficiency (%)	Agitation speed effect ^a (%)	Liquid volume effect ^b (%)	Liquid temperature effect ^c (%)
A	Cold	Low	Slow	99	-1.0	59	1.0
A replicate	Cold	Low	Slow	99			
B	Hot	Low	Slow	100	0.0	56	1.0
C	Cold	High	Slow	36	-8.0	59	4.0
C replicate	Cold	High	Slow	44			
D	Hot	High	Slow	44	-18	56	4.0
E	Cold	Low	Fast	100	-1.0	52	0.0
F	Hot	Low	Fast	100	0.0	38	0.0
G	Cold	High	Fast	48	-8.0	52	14
H	Hot	High	Fast	62	-18	38	14
Average =					-6.8	51	4.8

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

detergent, and mass of clothes. The second group involved an investigation of other factors: liquid temperature, liquid volume, and agitation speed. In order to focus on single-variable effects, detergent and clothes were not used for this second group of experiments.

For each group, the results of the factorial main effect analysis (see Section 3.7 for methodology) are given. To illustrate this analysis, the calculation of the main effect of detergent on acetone's stripping efficiency in factorial #1 is shown below.

Corresponding Experiments:		Difference in Stripping Efficiencies
Average (1 and 1 rep) to Average (3 and 3 rep) =		-1.0 %
2 to 4 =		6.0 %
5 to 7 =		-1.0 %
6 to 8 =		-13 %
Average	=	-2.2 %

As shown in Table 6-8, the difference in experimental response was listed twice, once for each corresponding experiment. Replicating the listing of each response, however, does not affect the average value for each variable. As shown in the example, the results for Experiments 1 and 1 replicate, and Experiments 3 and 3 replicate were averaged, respectively, before applying any factorial analyses. Tables 6-9 to 6-16 follow this same format.

Acetone stripping efficiencies are reported for each factorial group in Tables 6-8 and 6-9. For both groups of factorials, stripping efficiencies for acetone ranged from 3.1% to 36%. The highest stripping efficiency value was for the conditions of low water volume, no clothes or detergent, hot water, and slow agitation. The second highest value associated with the second factorial group was 31%, also associated with hot water, no clothes or detergent present, and low water volume. However, this value occurred during a fast agitation speed. It was expected that for similar operating conditions, experiments completed at a higher temperature would result in higher stripping efficiencies because of the corresponding increase in Henry's law constant. For the temperatures listed in Table 6-6, Henry's law constants for acetone ranged from 0.00085 $\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiments 7 and G at 18°C) to 0.0051 $\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiments 4 and D at 51°C).

The first factorial analysis for acetone stripping efficiencies was based on values calculated using Experiments 1 through 8. In keeping with these values, the highest main effect was 8.9% for the single variable factor of liquid temperature. The main effect from differences in liquid temperature was calculated by subtracting cold water stripping efficiencies from corresponding (similar amounts of clothing and detergent present) hot water stripping efficiencies. A positive

effect indicated an absolute increase in stripping efficiency with increasing water temperature. This result was expected, based on the increasing Henry's law constant as described above. When the experiments were grouped according to liquid temperature and the respective stripping efficiencies averaged, the following values resulted: 12% for cold water experiments (Experiments 1, 1 replicate, 3, 3 replicate, 5, and 7) and 24% for hot water experiments (Experiments 2, 4, 6, and 8).

A more practical way to group the experimental results was to combine the liquid temperature effects with using clothes in a wash or rinse (no detergent present) cycle. The average stripping efficiencies were 20% and 19% for cold water use during wash and rinse cycles, respectively, and 22% and 9.4% for hot water use during wash and rinse cycles, respectively.

The second factorial group also included liquid temperature as a factor (11% main effect). However, liquid volume had a slightly greater main effect, with a value of 15%. The main effect from differences in liquid volume was calculated by subtracting high water volume stripping efficiencies from low water volume stripping efficiencies. Thus, a positive 14% indicated an absolute increase in stripping efficiency with decreasing water volume. At lower water volumes, the total kinetic energy (TKE) resulting from agitation of the water surface increases, thereby increasing the potential for chemical volatilization.

When the second factorial results were grouped according to liquid volume, the following average stripping efficiencies resulted: 21% for low volume experiments and 7.3% for high volume experiments. Liquid temperature also had a significant impact on acetone stripping efficiencies. Grouping experiments according to volume and liquid temperature resulted in the following average values: 13% for low volume and cold water experiments, 34% for low volume and hot water experiments, 6.1% for high volume and cold water experiments, and 9.1% for high volume and hot water experiments.

As for all chemicals, the reported acetone stripping efficiencies represent a range of possible transfer efficiencies for different operating conditions. A better estimation of chemical

volatilization may be made using K_LA values reported in Section 6.2.4.3. These values were based on a well-mixed initial liquid-phase concentration, rather than the highest peak.

Washing machine wash/rinse cycle Experiments 1 (A), 3, and C were replicated. When the acetone stripping efficiencies for these three experiment were compared, the following relative differences were calculated: 71% for Experiments 1(A) and 1(A) replicate, 31% for Experiments 3 and 3 replicate, and 34% for Experiments C and C replicate.

Because of detergent interaction discussed in Section 6.2.3, only ethyl acetate results for the second factorial group are reported in this section. As shown in Table 6-10, *ethyl acetate stripping efficiencies* ranged from 5.1% to 48%. Again, the highest stripping efficiency corresponded to the conditions of low water volume, low agitation speed, and hot water. The highest main effect for ethyl acetate stripping efficiencies was liquid temperature, with a value of 18%. Grouping the stripping efficiencies according to liquid temperature, resulted in a cold water average of 9.1% and a hot water average of 27%. For the temperatures listed in Table 6-6, Henry's law constants for ethyl acetate ranged from $0.0037 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ to $0.016 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$.

The second highest factor on ethyl acetate stripping efficiencies was liquid volume, with a value of 17%. As with acetone, the stripping efficiencies for ethyl acetate may be grouped according to liquid volume and liquid temperature such that 12% is the average for cold water and low volume, 41% is the average for hot water and low volume, 6.1% is the average for cold water and high volume, and 14% is the average value for hot water and high volume.

Replicate experiments with ethyl acetate results included Experiments A and A replicate and C and C replicate. Stripping efficiencies were within 39% for Experiments A and A replicate and were identical for Experiments C and C replicate.

Toluene stripping efficiencies ranged from 24% to 99% for both factorial experimental groups (Tables 6-11 and 6-12). The highest stripping efficiency corresponded to conditions of hot water, low volume, no clothes or detergent present, and fast agitation. Again, hot water led

to higher stripping efficiencies. For temperatures listed in Table 6-6, Henry's law constants for toluene ranged from $0.22 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ to $0.57 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$.

Toluene stripping efficiencies exhibited a wide range of values depending on associated operating conditions. Thus, the factorial analysis was a useful tool in determining variable impacts. For the first factorial group, the variable with the single highest effect was liquid temperature at a value of 23%. Grouping stripping efficiencies according to liquid temperature resulted in an average value of 49% for cold water experiments and 70% for hot water experiments.

The clothes main effect was 15%, indicating that stripping efficiencies tended to decrease with clothes in the machine. This phenomenon was previously observed by Shepherd et al. (1996) for chloroform in washing machines, and is likely caused by suppression of turbulent kinetic energy by clothes in the washbasin. The cold water wash and rinse cycles with clothes had stripping efficiencies of 42% and 45%, respectively. The hot water wash and rinse cycles with clothes were characterized by higher stripping efficiencies of 62% and 56%, respectively.

Both the cold water and hot water wash and rinse cycles had lower stripping efficiencies than the averages calculated based on temperature. This difference may be attributed to the impact of detergent and clothes on stripping efficiencies. The detergent main effect was also 15%, indicating that stripping efficiencies tended to decrease for wash cycles. Surfactants present in detergent act to suppress chemical volatilization by increasing liquid-phase resistance to mass transfer. Thus, it is not coincidental that the presence of detergents has a greater effect on those tracers that were dominated by liquid-phase resistance to mass transfer (toluene, ethylbenzene, cyclohexane) than those dominated by gas-phase resistance to mass transfer (acetone).

The second factorial group was used to investigate the impacts of water temperature, water volume, and agitation speed. A wide range of values also characterizes this group of experiment results. For this group, the effects of liquid volume far exceeded the effects of temperature and agitation speed, with a value of 54%. Grouping experimental stripping efficiencies according to

liquid volumes resulted in an 80% average for low-volume experiments, and 29% average for high-volume experiments. Accounting for the second highest factor of liquid temperature further separated these averages. The average stripping efficiency for low volume and cold water was 69%, the average for low volume and hot water was 97%, the average for high volume and cold water was 26%, and the average for high volume and hot water was 33%. As a worst case scenario, operating at conditions of hot water and low water volume, virtually all of the toluene mass initially present in the washing machine basin would be emitted to room air. However, operating with conditions of high water volume with cold water, only 25% of the toluene mass would be emitted. Thus, using a 100% volatilization estimate would dramatically overestimate chemical emissions for several operating conditions.

Replicate experiment results for toluene had relative differences of 10% for Experiments 1(A) and 1(A) replicate, 3.0% for Experiments 3 and 3 replicate, and 7.4% for Experiments C and C replicate.

As discussed in Section 3.2.1, toluene and ethylbenzene have similar Henry's law constants and thus should yield similar volatilization results. As shown in Tables 6-13 and 6-14, *ethylbenzene stripping efficiencies* ranged from 24% to 99%. This range was similar in magnitude to the range of stripping efficiencies reported for toluene. Over 17 experiments, the average relative difference between toluene and ethylbenzene stripping efficiencies was 8.3%.

Main effect values for ethylbenzene were only slightly different from those for toluene. Again, for the first factorial group, liquid temperature had the dominant main effect on stripping efficiency, with a value of 21%. Contrary to results obtained for toluene, there was a difference in the magnitude of the main effect associated with clothes and detergent. In fact, detergent had a main effect value almost twice as high as that observed for clothes. Thus, there was a greater difference between wash and rinse cycles for this compound. However, ethylbenzene stripping efficiencies were similar for wash and rinse cycles at similar temperatures.

For the second factorial group, ethylbenzene again shared common main effects with toluene. For example, the main effect for liquid volume was 56% and by far exceeded other

main effect values. Grouping stripping efficiencies according to this one effect resulted in an average stripping efficiency of 83% for low liquid volume and 30% for high liquid volume, again a factor of three difference. Adding temperature effects to these averages resulted in values of 73% for low volume and cold water, 98% for low volume and hot water, 28% for high volume and cold water, and 33% for high volume and hot water.

Replicate experiment results for ethylbenzene stripping efficiencies were 10% for Experiments 1(A) and 1(A) replicate, 2.7% for Experiments 3 and 3 replicate, and 10% for Experiments C and C replicate.

Finally, *cyclohexane stripping efficiencies* ranged from 36% to 100% (see Tables 6-15 and 6-16). For similar experimental conditions, cyclohexane consistently had the highest stripping efficiency of the five experimental tracers. Experiments involving hot or cold water, fast or slow agitation, and low liquid volume resulted in stripping efficiencies of at least 99%. For the temperatures listed in Table 6-6, Henry's law constants for cyclohexane ranged from $5.8 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ to $16 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$.

Presence of clothes in the machine and water temperature had equal main effect magnitudes for cyclohexane in the first factorial group. Grouping cyclohexane stripping efficiencies according to these two factors resulted in the following averages: 89% for no clothes and cold water, 99% for no clothes and hot water, 79% for clothes and cold water, and 89% for clothes and hot water. Washing and rinsing clothes in cold water each led to a stripping efficiency of 79%. A stripping efficiency of 89% was observed for wash and rinse cycles involving clothes and hot water.

For factorial group #2, cyclohexane had a wider range of experimental results. This wider range derives primarily from the large main effect value for liquid volume. This effect was approximately seven times greater than the main effects for the other two variables. Grouping stripping efficiencies according to liquid volume resulted in an average value of 100% for low-volume experiments and 45% for high-volume experiments.

Replicate experiments had the following relative differences in results: 0% for Experiments 1(A) and 1(A) replicate, 7.6% for Experiments 3 and 3 replicate, and 20% for C and C replicate.

In general, the presence of clothes and/or detergent and using high water volumes resulted in reduced chemical stripping efficiencies. Accounting for these variable effects leads to significantly lower transfer efficiencies than the often assumed value of 100%.

6.2.4.3. K_LA Values

Values of K_LA for each chemical tracer are reported in Tables 6-17 to 6-25, using the same two factorial groups as for chemical stripping efficiencies. Again, the first factorial group was designed to investigate the effects of liquid temperature, use of detergent, and presence of clothes on K_LA . The second factorial group was designed to investigate the effects of liquid temperature, liquid volume, and agitation speed on K_LA . Values of K_LA for acetone and ethyl acetate were based on minimizing the residuals between the measured and predicted gas-phase data (see Section 3.6.2 for methodology). Values of K_LA for the remaining tracers were based on minimizing the residuals between the measured and predicted liquid-phase data. Tables 6-17 through 6-25 have a similar format to that of Tables 6-8 to 6-16, except that the main effects are based on values of K_LA .

Values of K_LA for acetone spanned nearly two orders of magnitude, ranging from 0.0075 to 0.31 L/minute (see Tables 6-17 and 6-18). The highest value corresponded to the experimental conditions of hot water, low water volume, no detergent or clothes present, and fast agitation. The highest value in the first factorial also corresponded to conditions of hot water, low water volume, no detergent or clothes present, but slow agitation.

The largest main effect for the first factorial group was liquid temperature, with a value of 0.10 L/minute. In a manner similar to that for stripping efficiency results, values of K_LA were grouped according to liquid temperature, resulting in the following average values: 0.024 L/minute for cold water experiments and 0.13 L/minute for hot water experiments.

Table 6-17. Acetone K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent ?	Clothes ?	K_LA (L/min)	Clothes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	Cold	No	no	0.069	0.023	0.037	0.25
1 replicate	Cold	No	no	0.024			
2	Hot	No	no	0.30	0.20	0.28	0.25
3	Cold	Yes	no	0.011	0.0022	0.037	0.012
3 replicate	Cold	Yes	no	0.0084			
4	Hot	Yes	no	0.022	-0.060	0.28	0.012
5	Cold	No	Yes	0.024	0.023	0.017	0.075
6	Hot	No	Yes	0.099	0.20	0.017	0.075
7	Cold	Yes	Yes	0.0075	0.0022	0.017	0.072
8	Hot	Yes	Yes	0.082	-0.060	0.017	0.072
Average =					0.042	0.087	0.10

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

Table 6-18. Acetone K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment. #	Liquid Temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect ^a (L/min)	Liq. volume effect ^b (L/min)	Liq. temp. effect ^c (L/min)
A	Cold	Low	Slow	0.069	-0.0010	0.025	0.25
A replicate	Cold	Low	Slow	0.024			
B	Hot	Low	Slow	0.30	-0.010	0.15	0.25
C	Cold	High	Slow	0.024	0.0010	0.025	0.13
C replicate	Cold	High	Slow	0.020			
D	Hot	High	Slow	0.15	0.064	0.15	0.13
E	Cold	Low	Fast	0.048	-0.0010	0.025	0.26
F	Hot	Low	Fast	0.31	-0.010	0.22	0.26
G	Cold	High	Fast	0.023	0.0010	0.025	0.063
H	Hot	High	Fast	0.086	0.064	0.22	0.063
Average =					0.013	0.11	0.18

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

Table 6-19. Ethyl acetate K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment. #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect ^a (L/min)	Liq. volume effect ^b (L/min)	Liq. temp. effect ^c (L/min)
A	Cold	Low	Slow	0.15	0.019	0.064	0.50
A replicate	Cold	Low	Slow	0.073			
B	Hot	Low	Slow	0.61	-0.21	0.36	0.50
C	Cold	High	Slow	0.053	-0.0090	0.064	0.20
C replicate	Cold	High	Slow	0.039			
D	Hot	High	Slow	0.25	0.12	0.36	0.20
E	Cold	Low	Fast	0.091	0.019	0.036	0.73
F	Hot	Low	Fast	0.82	-0.21	0.69	0.73
G	Cold	High	Fast	0.055	-0.0090	0.036	0.075
H	Hot	High	Fast	0.13	0.12	0.69	0.075
Average =					-0.020	0.29	0.38

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

Table 6-20. Toluene K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent ?	Clothes ?	K_LA (L/min)	Clothes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	Cold	No	no	9.4	7.5	6.3	6.7
1 replicate	Cold	No	no	7.1			
2	Hot	No	no	15	11	12	6.7
3	Cold	Yes	no	1.5	1.4	6.3	1.5
3 replicate	Cold	Yes	no	2.5			
4	Hot	Yes	no	3.5	1.4	12	1.5
5	Cold	No	Yes	0.84	7.5	0.26	3.1
6	Hot	No	Yes	3.9	11	1.8	3.1
7	Cold	Yes	Yes	0.58	1.4	0.26	1.5
8	Hot	Yes	Yes	2.1	1.4	1.8	1.5
Average =					5.3	5.0	3.2

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

Table 6-21. Toluene K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect ^a (L/min)	Liq. volume effect ^b (L/min)	Liq. temp. effect ^c (L/min)
A	Cold	Low	Slow	9.4	-2.7	5.5	6.7
A replicate	Cold	Low	Slow	7.1			
B	Hot	Low	Slow	15	-23	12	6.7
C	Cold	High	Slow	2.7	1.3	5.5	0.50
C replicate	Cold	High	Slow	2.9			
D	Hot	High	Slow	3.3	1.8	12	0.50
E	Cold	Low	Fast	11	-2.7	9.5	27
F	Hot	Low	Fast	38	-23	37	27
G	Cold	High	Fast	1.5	1.3	9.5	0
H	Hot	High	Fast	1.5	1.8	37	0
Average =					-5.7	16	8.6

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

Table 6-22. Ethylbenzene K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid temp.	Detergent ?	Clothes ?	K_LA (L/min)	Clothes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	Cold	No	no	10	8.0	6.7	7.9
1 replicate	Cold	No	no	8.1			
2	Hot	No	no	17	13	13	7.9
3	Cold	Yes	no	2.2	1.5	6.7	1.9
3 replicate	Cold	Yes	no	2.6			
4	Hot	Yes	no	4.3	2.1	13	1.9
5	Cold	No	Yes	1.1	8.0	0.17	2.9
6	Hot	No	Yes	4.0	13	1.8	2.9
7	Cold	Yes	Yes	0.93	1.5	0.17	1.3
8	Hot	Yes	Yes	2.2	2.1	1.8	1.3
Average =					6.1	5.3	3.5

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

Table 6-23. Ethylbenzene K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect ^a (L/min)	Liq. volume effect ^b (L/min)	Liq. temp. effect ^c (L/min)
A	Cold	Low	Slow	10	-2.9	6.0	7.9
A replicate	Cold	Low	Slow	8.1			
B	Hot	Low	Slow	17	-21	14	7.9
C	Cold	High	Slow	3.0	1.6	6.0	-0.20
C replicate	Cold	High	Slow	3.2			
D	Hot	High	Slow	2.9	1.2	14	-0.20
E	Cold	Low	Fast	12	-2.9	11	26
F	Hot	Low	Fast	38	-21	36	26
G	Cold	High	Fast	1.5	1.6	11	0.20
H	Hot	High	Fast	1.7	1.2	36	0.20
Average =					-5.3	17	8.5

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

Table 6-24. Cyclohexane K_LA values for washing machine wash/rinse cycle—Factorial #1

Experiment #	Liquid Temp.	Detergent ?	Clothes ?	K_LA (L/min)	Clothes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	Cold	No	No	24	21	15	22
1 replicate	Cold	No	No	23			
2	Hot	No	No	46	39	22	22
3	Cold	Yes	No	9.4	5.7	15	15
3 replicate	Cold	Yes	No	9.2			
4	Hot	Yes	No	24	18	22	15
5	Cold	No	Yes	2.9	21	-0.7	3.9
6	Hot	No	Yes	6.8	39	0.8	3.9
7	Cold	Yes	Yes	3.6	5.7	-0.7	2.4
8	Hot	Yes	Yes	6.0	21	0.8	2.4
Average =					21	9.2	11

^aClothes effect from full to none.

^bDetergent effect from 40 grams to none.

^cLiquid temperature effect from cold to hot.

Table 6-25. Cyclohexane K_LA values for washing machine wash/rinse cycle—Factorial #2

Experiment #	Liquid temp.	Liquid volume	Agitation speed	K_LA (L/min)	Agitation effect ^a (L/min)	Liq. volume effect ^b (L/min)	Liq. temp. effect ^c (L/min)
A	Cold	Low	Slow	24	-28	20	22
A replicate	Cold	Low	Slow	23			
B	Hot	Low	Slow	46	-48	42	22
C	Cold	High	Slow	3.4	1.4	20	0.2
C replicate	Cold	High	Slow	5.2			
D	Hot	High	Slow	4.5	-1.4	42	0.2
E	Cold	Low	Fast	52	-28	49	42
F	Hot	Low	Fast	94	-48	88	42
G	Cold	High	Fast	2.9	1.4	49	3.0
H	Hot	High	Fast	5.9	-1.4	88	3.0
Average =					-19	50	17

^aAgitation speed effect from fast to slow.

^bLiquid volume effect from high to low.

^cLiquid temperature effect from cold to hot.

The second largest main effect on acetone K_LA values was use of detergent, with a value of 0.087 L/minute. Regrouping experiments according to water temperature and detergent use resulted in the following average K_LA values: 0.039 L/minute for cold water and no detergent, 0.20 L/minute for hot water and no detergent, 0.0090 L/minute for cold water and detergent, and 0.052 L/minute for hot water and detergent. As shown by these average values, operating conditions influence the appropriate selection of K_LA .

The highest main variable effect for the second factorial group was 0.18 L/minute, again for liquid temperature. Grouping acetone results according to this main effect resulted in an average value of K_LA of 0.035 L/minute for cold water experiments and 0.21 L/minute for hot water experiments. The dominance of liquid temperature effects on acetone K_LA values for both factorial groups illustrates the importance of this factor.

Values of K_LA for replicate experiments were also compared. For experiments 1(A) and 1(A) replicate, the relative difference in K_LA values was 97%. For Experiments 3 and 3 replicate, the relative difference in values of K_LA was 27%. Finally for Experiments C and C replicate, the relative difference in values of K_LA was 18%. For wash/rinse cycles, acetone had relatively low values of K_LA , which resulted in larger relative differences. For example,

acetone's K_LA values for Experiments 1 (A) and 1 (A) replicate differed by only 0.0445 L/minute, which resulted in a 97% relative difference.

Measured and predicted liquid-phase and gas-phase concentrations for Experiment 6 are presented in Figure 6-6, and are representative of other experiments. The operating conditions used in Experiment 6 were hot water, low water volume, slow agitation speed, clothes, and rinse cycle (no detergent present). As described in Section 6.2.3.3, values of K_LA for acetone were determined by fitting the gas-phase predicted concentrations to the measured gas-phase data for points collected after 180 seconds into the experiment. As shown in Figure 6-6, the experimental time of 180 seconds was set to time 0, and the remaining data were also shifted by 180 seconds. The best-fit value of K_LA for acetone for this experiment was 0.099 L/minute. The corresponding hot water wash cycle K_LA was 0.082 L/minute. When cold water was used, the associated wash and rinse cycle values of K_LA were 0.0075 L/minute and 0.024 L/minute, respectively.

At 180 seconds into each experiment (zero in Figure 6-6), the liquid-phase concentration of acetone was observed to slowly decrease because of the relatively low value of K_LA . Figure 6-7

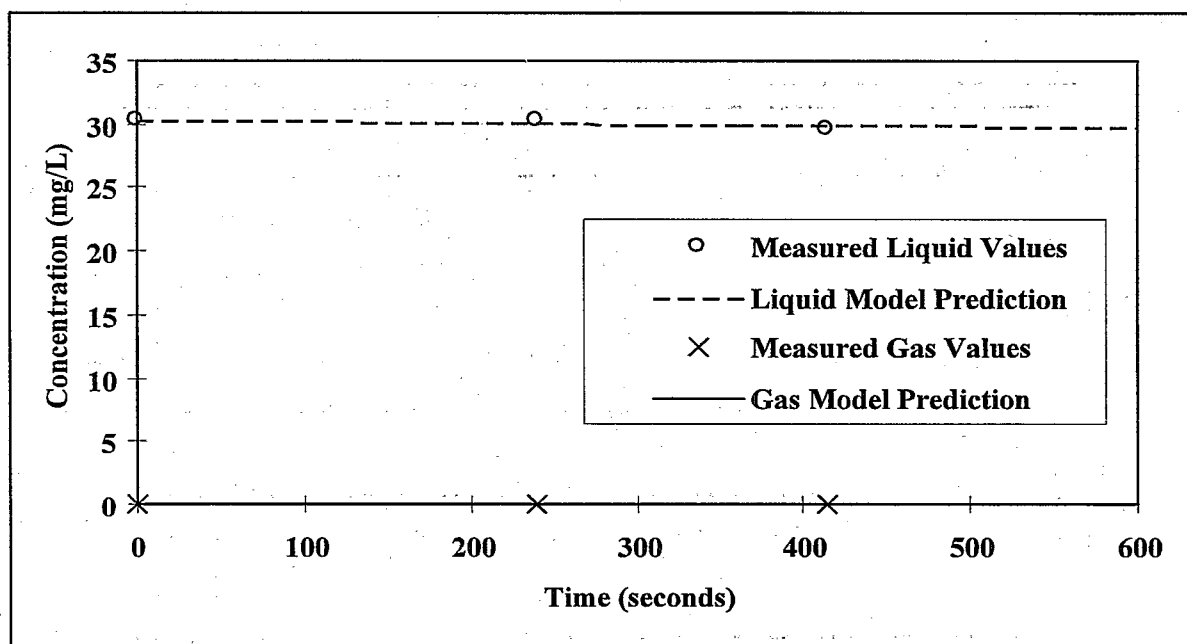


Figure 6-6. Acetone concentrations from experiment 6.

shows a magnification of the y-axis in Figure 6-6 to illustrate the general decrease in the gas-phase concentration of acetone during the experiment. The high ventilation rate for washing machines precluded an approach to chemical equilibrium for all tracers, including acetone. Values of $K_L A$ for ethyl acetate ranged from 0.039 to 0.82 L/minute for factorial group #2, as shown in Table 6-19. Again, the detergent effect on ethyl acetate's elution from the GC negated the use of factorial #1 experiments in the data analysis. The highest value of $K_L A$ was for the experimental conditions of hot water, low water volume, no clothes or detergent present, and fast agitation. As with acetone, the largest main effect was liquid temperature with a value of 0.38 L/minute. The average cold water value of $K_L A$ for ethyl acetate was 0.077 L/minute, and the average hot water value was 0.45 L/minute. Based on the factorial analysis, values of $K_L A$ for ethyl acetate tended to increase with increasing temperature and agitation speed, and decrease with higher water volumes.

Replicate values of $K_L A$ for ethyl acetate had a relative difference of 69% for Experiments A and A replicate, and 30% for Experiments C and C replicate. Again, the relatively small values of $K_L A$ led to larger relative differences than generally observed for toluene, ethylbenzene, and cyclohexane.

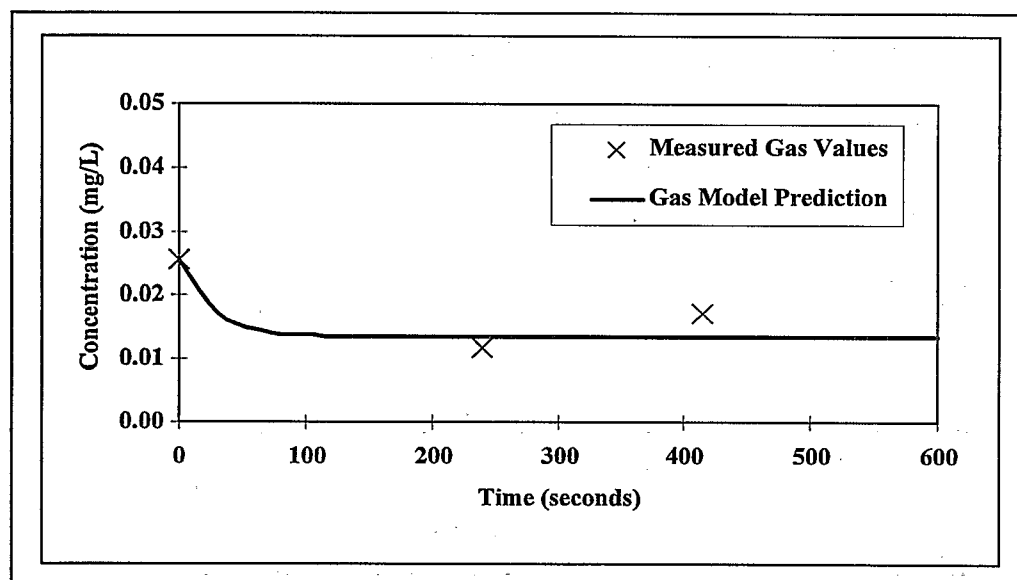


Figure 6-7. Amplification of Figure 6-6 for acetone gas-phase data.

As shown in Tables 6-20 and 6-21, values of K_LA for toluene ranged from 0.58 to 38 L/minute, a range covering two orders of magnitude. Similar to the acetone and ethyl acetate experiments, the operating conditions of hot water, low water volume, no detergent or clothes, and fast agitation resulted in the highest value of K_LA . Unlike acetone and ethyl acetate, the largest main effect for toluene associated with factorial #1 was presence of clothes, with a value of 5.3 L/minute. Detergent's main effect was similar to the clothes effect at 5.0 L/minute. As with stripping efficiency, both of these factors appeared to decrease values of K_LA for toluene.

Grouping values of K_LA for toluene according to use of detergent and clothes in the experiment resulted in the following averages: 11 L/minute for no clothes or detergent present, 2.5 L/minute for only detergent present, 2.4 L/minute for only clothes present, and 1.3 L/minute for both clothes and detergent present. Individually, detergent and clothes had a similar effect on values of K_LA for toluene. These effects appeared to be compounded when both were present in the machine to lower K_LA .

For factorial #2, the liquid volume main effect (16 L/minute) was approximately three times as high as the main effect associated with agitation speed (-5.7 L/minute), and approximately two times as high as the main effect associated with liquid temperature (8.6 L/minute). The average value of K_LA was 2.4 L/minute for a high water volume as opposed 16 L/minute for a low liquid volume.

Values of K_LA for replicate experiments were also compared. For experiments 1(A) and 1(A) replicate, the relative difference in values of K_LA was 28%. For Experiments 3 and 3 replicate, the relative difference in values of K_LA was 50%. Finally, for Experiments C and C replicate, the relative difference in values of K_LA was 7.1%.

Toluene results for Experiment 6 are presented in Figure 6-8. Toluene K_LA values were determined by fitting the predicted liquid concentrations to the measured liquid-phase concentrations. The best-fit K_LA value for this experiment was 3.9 L/minute. The y-axis in Figure 6-8 is magnified to illustrate the general decrease in toluene gas-phase concentration after

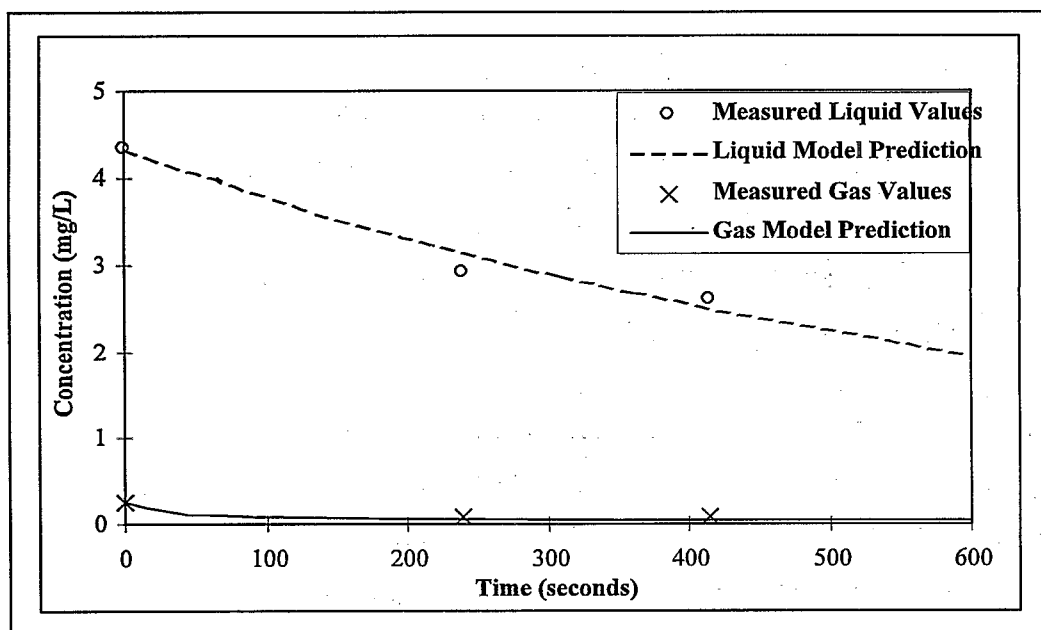


Figure 6-8. Toluene concentrations for Experiment 6.

the initial 180 seconds of the experiment. Like other chemicals, the general shape of the gas-phase curve for the entire experiment included an increase in gas-phase concentration to a peak, followed by a decrease in gas-phase concentration as shown in Figure 6-9.

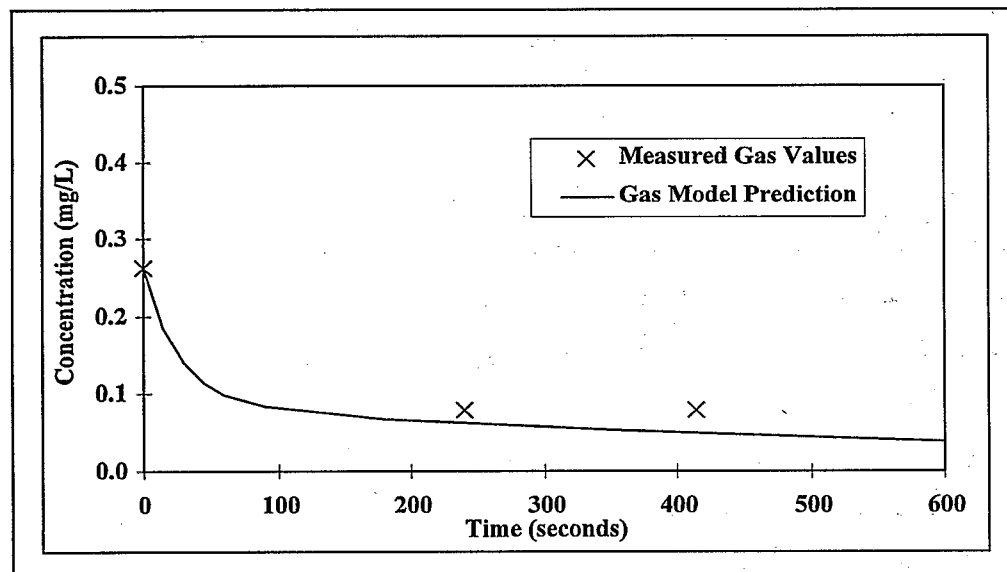


Figure 6-9. Magnification of Figure 6-8 to illustrate toluene's gas-phase concentration over time.

Values of $K_L A$ for ethylbenzene ranged from 0.93 to 38 L/minute for both factorial groups (see Tables 6-22 and 6-23). Again, this range is similar in magnitude to that of toluene, despite some difference in Henry's law constant at higher temperatures. Ethylbenzene also had main effects similar to those calculated for toluene. Based on these main effects, the average ethylbenzene $K_L A$ value for experiments using no detergent or clothes was 12 L/minute. When detergent or clothes were added to the machine, the average values of $K_L A$ were 3.0 L/minute and 2.6 L/minute, respectively. Finally, when both clothes and detergent were added to the machine together, the average value of $K_L A$ was 1.6 L/minute.

Values of $K_L A$ for ethylbenzene in the second factorial group were most dependent on liquid volume. An average $K_L A$ for ethylbenzene during high water volume experiments was 2.5 L/minute, and an average low water volume $K_L A$ for ethylbenzene was 17 L/minute, a difference of a factor of 7.

Comparing results for replicate experiments yielded the following relative differences in values of $K_L A$ for ethylbenzene: 21% for Experiments 1(A) and 1(A) replicate, 17% for Experiments 3 and 3 replicate, and 6.5% for Experiments C and C replicate.

Ethylbenzene data for Experiment 6 are plotted in Figure 6-10. Liquid-phase and gas-phase curves have the same shape as those for toluene. The ethylbenzene $K_L A$ value for this plot was 4.0 L/minute.

Finally, values of $K_L A$ for cyclohexane ranged from 2.9 L/minute to 94 L/minute for both factorial groups listed in Tables 6-24 and 6-25. Cyclohexane has a relatively high Henry's law constant compared with other tracers, which led to consistently higher values of $K_L A$. For these experiments, there appeared to be significant gas-phase resistance to mass transfer evident by the wide range of results between tracers.

The greatest main effect for cyclohexane based on factorial #1 was the presence of clothes. The main effect value of 21 L/minute for clothes was twice as high as the main effect associated with detergent or water temperature. For the second factorial, the largest main effect was again

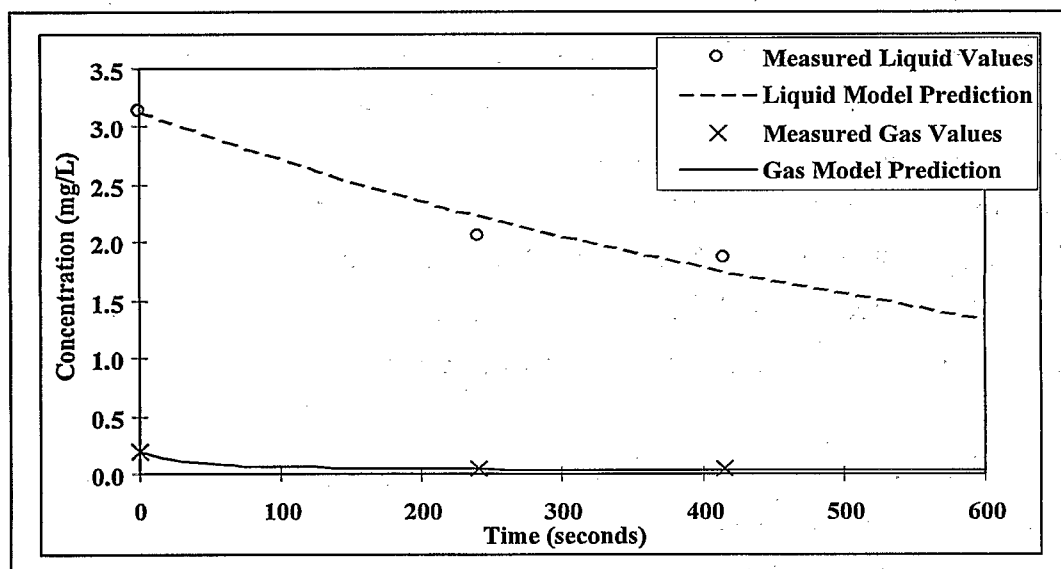


Figure 6-10. Ethylbenzene concentrations for Experiment 6.

water volume. Average values of K_LA for low water volume and high water volume were 48 L/minute and 4.4 L/minute, respectively, a difference of a factor of 10 between averages.

Comparing results for replicate experiments yielded the following relative differences in values of K_LA for cyclohexane: 4.3% for Experiments 1(A) and 1(A) replicate, 2.2% for Experiments 3 and 3 replicate, and 42% for Experiments C and C replicate.

Cyclohexane experimental data are plotted in Figure 6-11 for Experiment 6. The liquid-phase curve shown in Figure 6-11 has a steeper slope than observed for toluene and ethylbenzene. The value of K_LA for this experiment was 6.8 L/minute for cyclohexane. The gas-phase curve followed the same shape as for the other tracers.

6.2.4.4. Liquid- and Gas-Phase Mass Transfer Coefficients

To apply the reported values of K_LA to other chemicals, it is necessary to separate K_LA into liquid- and gas-phase values (i.e., k_lA , and k_gA), and to determine k_g/k_l for each experiment. For this system, values of k_g/k_l should not vary significantly between volatile chemicals. Values of k_lA and k_gA for each chemical tracer are listed in Tables 6-26 and 6-27. A single value of

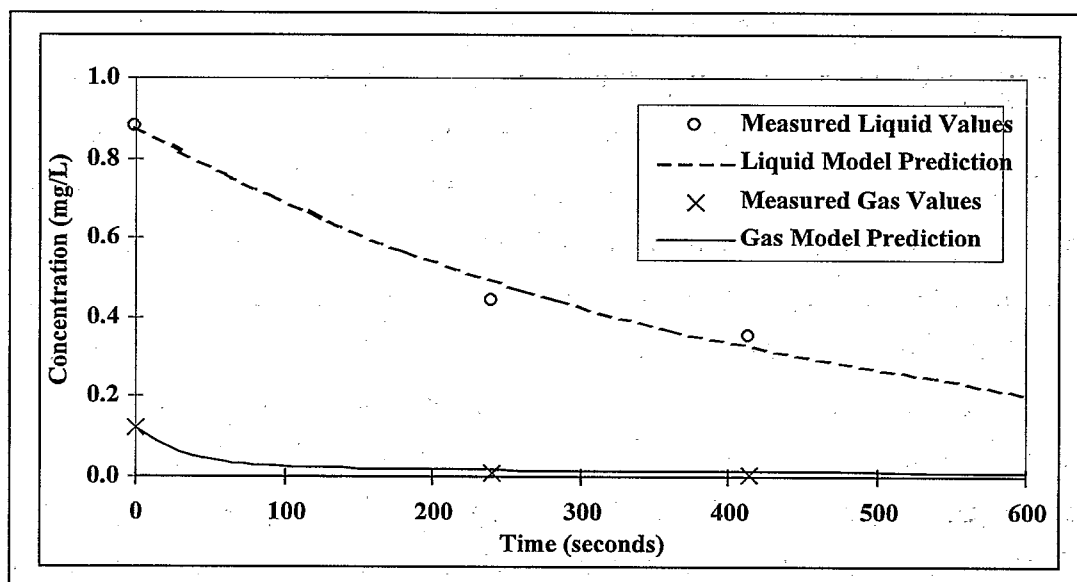


Figure 6-11. Cyclohexane concentrations for Experiment 6.

k_g/k_l is presented based on all chemical tracer experimental values of K_LA and physicochemical properties, as described in Section 3.6.3.

The impact of operating conditions on k_lA and k_gA was investigated for both factorial groups as outlined in Section 3.7. For factorial group #1, the most significant factor affecting k_lA for all chemicals was presence of clothes. This result is similar to that of K_LA , where the most significant factor was presence of clothes for all chemicals except acetone (most affected by temperature). The most significant factor affecting k_gA for all chemicals was use of detergent. For factorial group #2, the most significant factor affecting k_lA and k_gA for all chemicals was water volume. These results for toluene, ethylbenzene, and cyclohexane are similar to those for K_LA . The values of K_LA for acetone and ethyl acetate were more significantly affected by temperature. As seen with the shower factorial analysis, there was typically less dependence on temperature for k_gA than for k_lA .

As shown in Tables 6-26 and 6-27, the ratio of k_g/k_l for washing machine wash/rinse cycles ranged from 0.13 to 8.6, with an average value of 2.2 for factorial group #1 and 2.4 for factorial group #2. These are relatively low values of k_g/k_l and are similar in magnitude to values reported by Hsieh et al. (1994) for diffused bubble aeration.

Liquid- and gas-phase mass transfer coefficients may also be used to determine the relative importance of liquid- and gas-phase resistances to mass transfer for specific chemicals and operating conditions. As shown in Equation 2.5, the overall resistance to mass transfer ($1/K_L A$) may be written as the sum of liquid-phase resistance to mass transfer ($1/k_L A$) and gas-phase resistance to mass transfer ($1/k_g A \cdot H_c$). These resistances are shown graphically in Figure 6-12 for each chemical (except ethyl acetate) in Experiment 6. The operating conditions for Experiment 6 included hot water, low water volume, clothes, no detergent, and slow agitation. As shown in Figure 6-12, resistance to mass transfer is predominantly gas-phase resistance dominated for acetone. In fact, the y-axis was adjusted for this plot, because acetone's overall resistance to mass transfer was much higher (9.8 minutes/L) than the other three chemicals. Although toluene and ethylbenzene had similar overall resistances to mass transfer for this experiment, their respective liquid- and gas-phase resistances to mass transfer were distributed differently. Gas-phase resistance to mass transfer was slightly greater than liquid-phase resistance for toluene. With a higher Henry's law constant for this experiment, gas-phase resistance to mass transfer was smaller than liquid-phase resistance for ethylbenzene. Finally, gas-phase resistance to mass transfer was insignificant for cyclohexane.

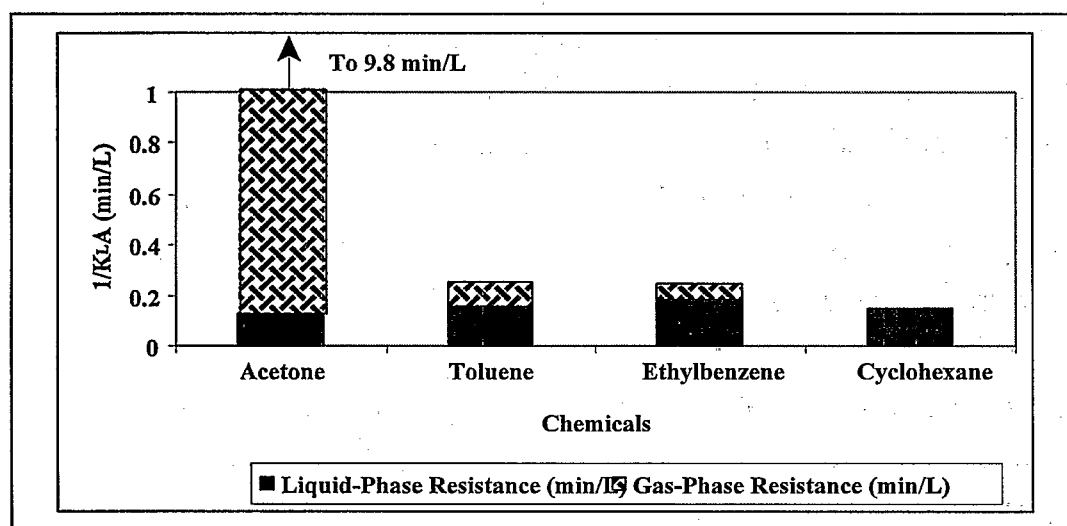


Figure 6-12. Liquid and gas-phase resistances to mass transfer for Experiment 6.

6.2.4.5. Mass Closure

For washing machine wash/rinse cycle experiments, mass closure for each chemical was calculated using Equation 3.10 and based on liquid- and gas-phase measurements collected during the same period in which values of K_LA were determined. Mass closure was reported in terms of the percentage of mass recovered based on initial total mass.

Values of mass closure for acetone ranged from 95% to 104%, with an average value of 99% for all 17 experiments. Percentages representing mass closure for ethyl acetate ranged from 98% to 114%, with an average value of 104% for applicable experiments (factorial #2 experiments). Mass closure values for toluene ranged from 65% to 135%, with an overall average of 89%. Ethylbenzene mass closure percentages ranged from 49% to 132%, with an overall average of 83%. Finally, cyclohexane had a mass closure range of 27% to 137%, with an average overall value of 72%.

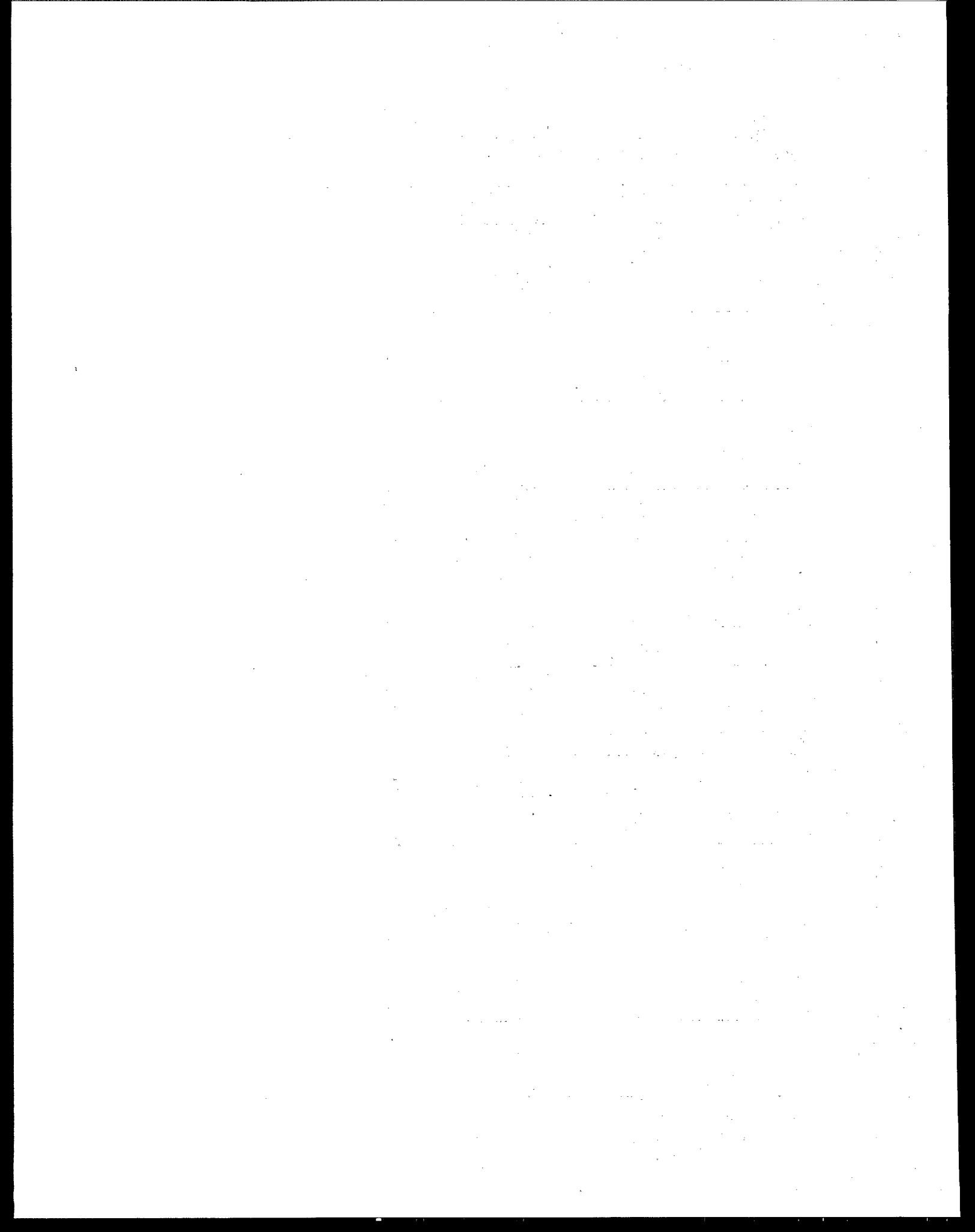
As discussed in Section 4.4.4, mass closure for more volatile chemicals (toluene, ethylbenzene, and cyclohexane) may be affected by differences in liquid-phase calibration curves based on tracer bag ages. Again, the actual calibration slope does not affect determination of chemical stripping efficiencies or values of K_LA . It does, however, affect determination of mass closure for each chemical because of the relation between gas- and liquid-phase mass. As shown in Section 4.4.4 for showers, improving the liquid-phase calibration curve resulted in as much as a 15% improvement for toluene mass closure values, a 30% improvement for ethylbenzene values, and 39% improvement for cyclohexane values.

Table 6-26. Liquid- and gas-phase mass transfer coefficients for washing machine wash/rinse cycle experiments—Factorial #1

Experiment #	Chemical	$k_l A$ (L/min)	$k_g A$ (L/min)	k_g/k_l
1	A	29	57	1.9
	T	27	53	
	EB	28	54	
	C	26	50	
1 replicate	A	24	22	0.92
	T	38	35	
	EB	40	36	
	C	26	34	
2	A	56	67	1.2
	T	38	46	
	EB	31	37	
	C	49	58	
3	A	13	10	0.74
	T	9.6	7.1	
	EB	12	9.2	
	C	11	8.4	
3 replicate	A	9.3	7.5	0.81
	T	15	12	
	EB	15	12	
	C	11	8.8	
4	A	32	4.3	0.13
	T	49	6.6	
	EB	31	4.2	
	C	34	4.6	
5	A	2.9	24	8.6
	T	1.3	11	
	EB	1.6	13	
	C	3.0	25	
6	A	7.7	21	2.8
	T	6.5	18	
	EB	5.4	15	
	C	6.9	19	
7	A	5.6	9.0	1.6
	T	2.2	3.6	
	EB	3.6	5.7	
	C	4.0	6.4	
8	A	5.9	18	3.1
	T	3.4	11	
	EB	2.9	8.9	
	C	6.2	19	

Table 6-27. Liquid-and gas-phase mass transfer coefficients for washing machine wash/rinse cycle experiments—Factorial #2

Experiment #	Chemical	$k_l A$ (L/min)	$k_g A$ (L/min)	k_g/k_l
A	A	40	57	1.4
	EA	23	32	
	T	34	49	
	EB	34	49	
	C	26	37	
A replicate	A	30	22	0.74
	EA	23	17	
	T	46	34	
	EB	47	35	
	C	27	20	
B	A	62	67	1.1
	EA	41	45	
	T	41	44	
	EB	33	36	
	C	49	53	
C	A	6.4	24	3.7
	EA	3.4	12	
	T	5.6	21	
	EB	6.1	23	
	C	3.6	13	
C replicate	A	9.7	20	2.1
	EA	4.8	9.5	
	T	8.8	18	
	EB	9.1	19	
	C	5.6	12	
D	A	6.0	30	5.1
	EA	3.5	18	
	T	4.4	23	
	EB	3.4	17	
	C	4.5	23	
E	A	99	49	0.50
	EA	45	22	
	T	103	51	
	EB	110	55	
	C	68	34	
F	A	120	69	0.58
	EA	103	59	
	T	161	92	
	EB	101	58	
	C	105	61	
G	A	4.2	27	6.4
	EA	2.4	15	
	T	2.5	16	
	EB	2.6	17	
	C	3.0	19	
H	A	6.3	18	2.8
	EA	3.2	8.8	
	T	2.5	7.0	
	EB	2.2	6.3	
	C	6.1	17	



7. BATHTUB EXPERIMENTS

Three primary activities associated with bathtub operation can cause chemicals originating in tap water to volatilize: (1) when water flows through a tub spout with an open drain (flow-through), (2) when water fills the tub with the drain closed (fill), and (3) when the tub is filled with water (surface volatilization). Bathtub experiments were divided into these three groups. Bathtub flow-through experiments are described in Section 7.1, fill experiments are discussed in Section 7.2, and surface volatilization experiments are presented in Section 7.3.

7.1. BATHTUB FLOW-THROUGH EXPERIMENTS

7.1.1. Experimental System

The same shower/bathtub unit described in Section 4.1 was used for all bathtub experiments. For flow-through experiments, the system had the same modifications and sample locations as the shower system. As shown in Figure 7-1, the only difference was that the washing machine contents were pumped through the bathtub spout rather than the showerhead.

7.1.2. Experimental Design

Similar to shower experiments, bathtub flow-through experiments were designed to last 8 minutes. Experimental variables were limited to water temperature and liquid flowrate. To test all combinations of these conditions, four experiments and one replicate experiment were completed.

7.1.3. Source-Specific Methodology

Bathtub flow-through experiments followed the same experimental methodology as for shower experiments (see Section 4.3).

7.1.3.1. Sample Schedule

It was expected that flow-through experiments would have less chemical volatilization than shower experiments. Therefore, 11 gas samples were collected for 1 minute instead of 30 seconds. In order to collect liquid samples at the mid point of gas sample collection times, the

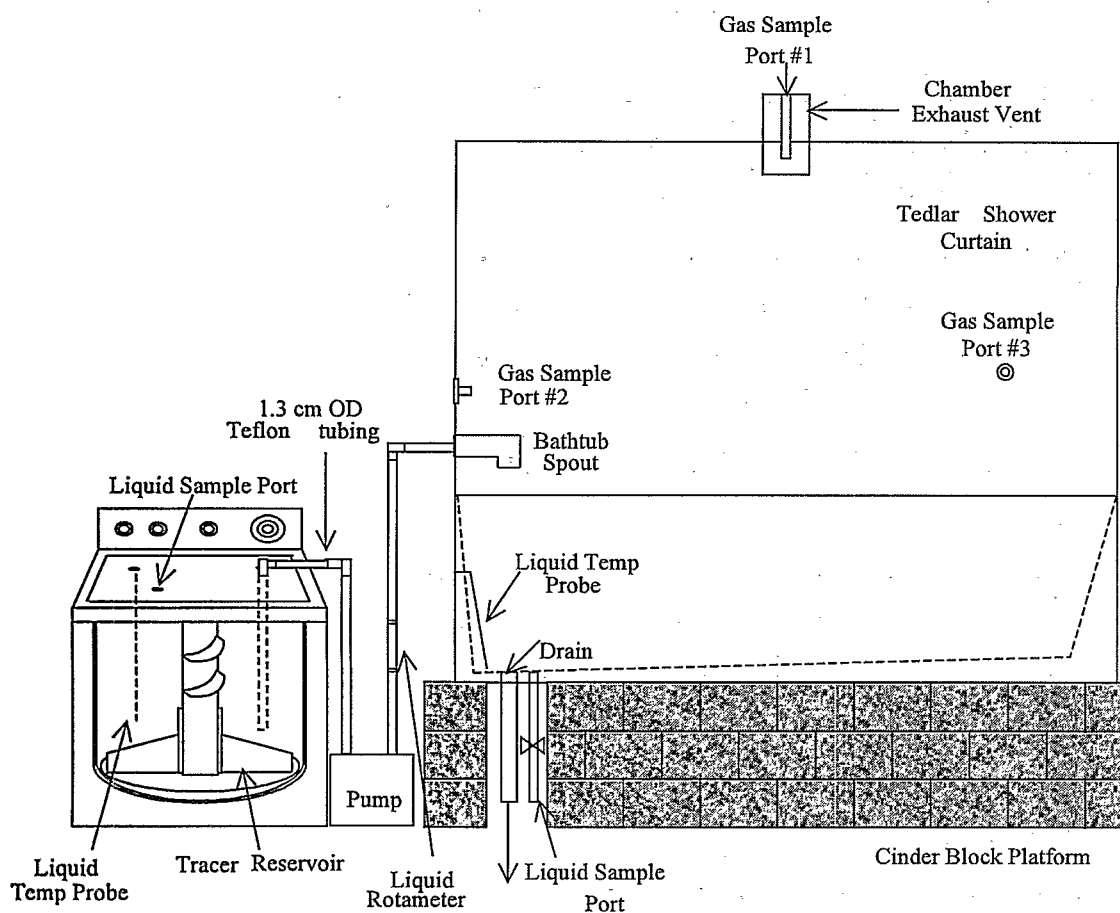


Figure 7-1. Bathtub flow-through experimental system.

liquid sample schedule was adjusted to 0.5, 1.5, two samples at 4.25 and 7.5 minutes. A nine liquid samples were collected for each experiment.

7.1.3.2. Ventilation Rate

Prediction of bathtub flow-through ventilation rates followed the same procedure developed for showers (see Section 4.3.2).

7.1.3.3. Parameter Estimation

The only difference between the parameter estimation for bathtub flow-through experiments and that for shower experiments (see Section 4.3.3) was the method to predict values of K_LA for

acetone. For showers, values of $K_L A$ for acetone were predicted based on minimizing the square of the normalized residual between measured and predicted liquid concentrations. For bathtubs, volatilization of acetone was near the average duplicate liquid sample error (see Section 3.5.1), such that the value of $K_L A$ was determined using gas-phase data. As for showers, values of $K_L A$ for the remaining tracers were based on liquid-phase data.

7.1.4. Bathtub Flow-Through Results

Six flow-through experiments were completed for which chemical stripping efficiencies and mass transfer coefficients ($K_L A$, $k_l A$, $k_g A$, and k_g/k_l) were determined. In addition to these results, the effects of liquid temperature and liquid flowrate on chemical volatilization are described in this section.

The operating conditions for each flow-through experiment are listed in Table 7-1.

7.1.4.1. Chemical Stripping Efficiencies

Chemical stripping efficiencies (η) are reported in Table 7-2. Stripping efficiencies for each chemical were based on liquid-phase measurements.

Acetone stripping efficiencies ranged from 1.7% to 5.3%. The highest value corresponded to the conditions of high flowrate and warm water. In fact, the two experiments completed with warm water led to the highest stripping efficiencies for acetone. Grouping stripping efficiencies according to water temperature and averaging them resulted in a cold water average of 2.9% and a warm water average of 4.9%.

Table 7-1. Bathtub flow-through operating conditions

Experiment #	Liquid temperature (°C)	Liquid flowrate (L/min)	Gas flowrate (L/min)	ACH (1/hr)
1	22	9.1	355	12
1 replicate	23	9.1	345	12
2	36	9.1	359	12
3	25	6.1	350	12
4	36	6.1	361	12
4 replicate	37	6.1	365	13

Table 7-2. Chemical stripping efficiencies (η) for experimental bathtub flow-through experiments

Experiment#	Liquid temp.	Liquid flowrate	Acetone η (%)	Ethyl acetate η (%)	Toluene η (%)	Ethylbenzene η (%)	Cyclohexane η (%)
1	Cold	High	3.8	6.1	26	27	28
1 rep	Cold	High	3.1	4.7	24	24	29
2	Warm	High	5.3	11	38	39	38
3	Cold	Low	1.7	4.5	22	22	22
4	Warm	Low	4.6	14	30	29	27
4 rep	Warm	Low	4.8	10	38	38	41

Ethyl acetate stripping efficiencies ranged from 4.5% to 14% and followed the same trends as acetone. A cold water average stripping efficiency for ethyl acetate was 5.1% and a warm water average stripping efficiency was 12%. The trend of increasing stripping efficiency with increasing temperature is primarily caused by the resulting increase in Henry's law constant for each chemical.

The stripping efficiencies for toluene, ethylbenzene, and cyclohexane were of similar magnitude. The ranges of stripping efficiencies for each chemical were 22% to 38% for toluene, 22% to 39% for ethylbenzene, and 22% to 41% for cyclohexane. The fact that toluene and ethylbenzene results were similar was not surprising given their similar Henry's law constants. For the range of temperatures listed in Table 7-1, toluene had Henry's law constants of $0.25 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiment 1) to $0.39 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiment 4), and ethylbenzene had Henry's law constants of $0.28 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiment 1) to $0.60 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiment 4). The fact that cyclohexane also had results similar to toluene and ethylbenzene indicated that there was not significant gas-phase resistance to mass transfer for the more volatile chemicals for this system. For the temperatures listed in Table 7-1, cyclohexane had significantly higher Henry's law constants ($6.6 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ [Experiment 1] to $11 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ [Experiment 4]) than did either toluene or ethylbenzene.

The temperature-dependent average stripping efficiencies for toluene, ethylbenzene, and cyclohexane were as follows: cold water averages were 24%, 24%, and 26%, respectively; and warm water averages were 35% for all three chemicals.

Bathtub flow-through Experiment 1 and Experiment 4 were repeated and reported as Experiment 1 replicate and Experiment 4 replicate, respectively. The relative difference between stripping efficiencies determined for Experiment 1 and Experiment 1 replicate for each chemical was 20% for acetone, 26% for ethyl acetate, 8.0 % for toluene, 12% for ethylbenzene, and 3.5% for cyclohexane. The relative difference between stripping efficiencies determined for Experiment 4 and Experiment 4 replicate for each chemical was 4.3% for acetone, 33% for ethyl acetate, 24% for toluene, 27% for ethylbenzene, and 41% for cyclohexane.

7.1.4.2. K_LA Values

Values of K_LA for all chemicals are reported in Table 7-3. Values of K_LA for acetone were based on gas-phase data. Values of K_LA for ethyl acetate, toluene, ethylbenzene, and cyclohexane were based on liquid-phase data.

The highest values of K_LA for acetone and ethyl acetate were associated with warm water experiments. Values of K_LA for acetone ranged from 0.11 to 0.54 L/minute. The cold water average value of K_LA was 0.15 L/min and the warm water average was 0.48 L/min. Values of K_LA for ethyl acetate ranged from 0.32 to 1.2 L/minute. The temperature dependent averages of K_LA for ethyl acetate were 0.48 L/min for cold water and 1.0 L/min for warm water.

The highest values of K_LA for toluene, ethylbenzene, and cyclohexane were for the conditions of high flowrate and warm water. However, experiments using cold water and a high flowrate also resulted in higher values of K_LA . Because the range of values of K_LA was so

Table 7-3. Values of K_LA for bathtub flow-through experiments

Experiment #	Liquid temp.	Liquid flowrate	Acetone K_LA (L/min)	Ethyl acetate K_LA (L/min)	Toluene K_LA (L/min)	Ethylbenzene K_LA (L/min)	Cyclohexane K_LA (L/min)
1	Cold	High	0.11	0.64	2.9	2.9	3.1
1 rep	Cold	High	0.15	0.49	2.4	2.4	2.9
2	Warm	High	0.54	1.2	4.5	4.5	5.1
3	Cold	Low	0.18	0.32	1.6	1.5	1.7
4	Warm	Low	0.43	1.1	2.2	2.1	1.9
4 rep	Warm	Low	0.46	0.79	2.9	2.9	3.2

narrow for these compounds, an overall average is reported here. Values of K_LA for toluene ranged from 1.6 to 4.5 L/minute, with an overall average of 2.8 L/minute. Values of K_LA for ethylbenzene ranged from 1.5 to 4.5 L/minute, with an overall average of 2.7 L/minute. Finally, values of K_LA for cyclohexane ranged from 1.7 L to 5.1 L/minute, with an overall average of 3.0 L/minute.

Mass transfer data for bathtub flow-through experiments may be presented in the same format as shower experimental data (see Section 4.4.2). A representative plot is shown in Figure 7-2 for toluene and Experiment 4 replicate. The operating conditions used in Experiment 4 replicate were warm water and low flowrate. As shown in Figure 7-2, each experimental period consisted of a liquid sample collected from the tracer reservoir, an outlet liquid sample, and a gas sample. For each period, the bathtub outlet concentration in both the liquid and gas phases may be estimated using the mass balance models (Equations 2.28 and 2.30). To determine the best K_LA value for the model, the residuals between the measured and predicted concentrations were minimized using the method described in Section 3.6.2. For toluene, the residual between liquid-phase values was minimized, resulting in a value of 2.9 L/minute for Experiment 4 replicate.

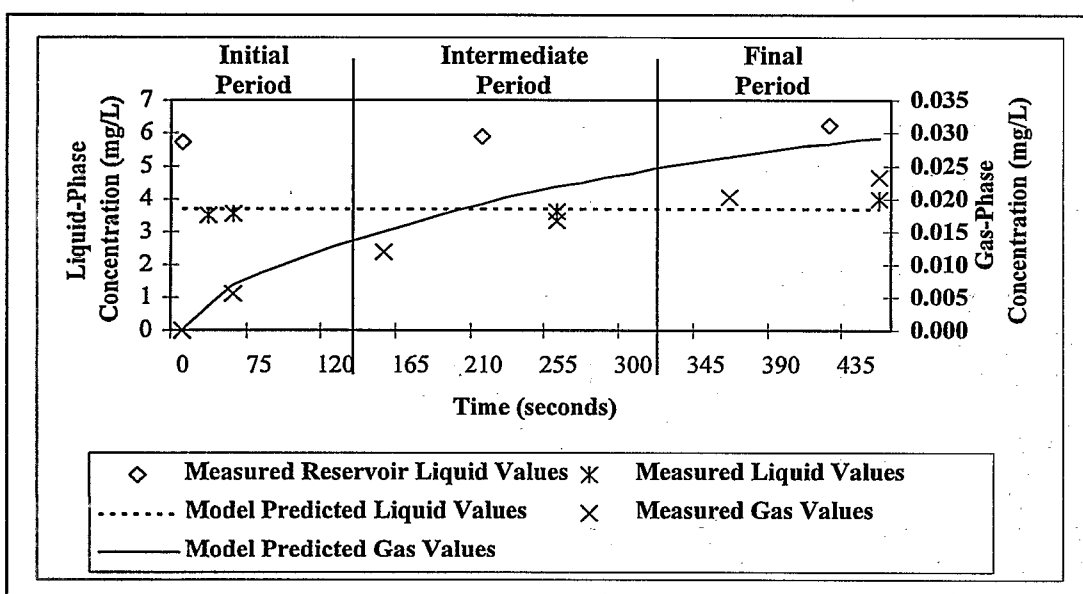


Figure 7-2. Toluene experimental data for Experiment 4 replicate.

7.1.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

Values of $K_L A$ for each chemical were separated into the components of $k_l A$ and $k_g A$ using Equation 2-5 and a value of k_g/k_l determined for each specific experiment (see Sections 3.6.3 and 3.6.4 for methodology). Values of $k_l A$ and $k_g A$ are reported in Table 7-4 for each chemical in addition to values of k_g/k_l for each experiment.

For bathtub flow-through experiments, values of k_g/k_l ranged from 37 to 96. In general, values of $k_l A$ and $k_g A$ for each chemical were similar in magnitude. The ratio of k_g/k_l was higher at low flowrates (average $k_g/k_l = 71$) than at high flowrates (average $k_g/k_l = 41$).

Table 7-4. Liquid- and gas-phase mass transfer coefficients for bathtub flow-through experiments

Experiment #	Chemical	$k_l A$ (L/min)	$k_g A$ (L/min)	k_g/k_l
1	A	2.9	108	37
	EA	4.5	168	
	T	3.2	117	
	EB	3.1	117	
	C	3.1	115	
1 replicate	A	3.2	136	43
	EA	3.0	126	
	T	2.6	111	
	EB	2.6	109	
	C	2.9	126	
2	A	6.0	249	42
	EA	4.9	205	
	T	4.8	198	
	EB	4.7	196	
	C	5.1	211	
3	A	2.4	159	66
	EA	1.3	86	
	T	1.7	110	
	EB	1.6	106	
	C	1.7	110	
4	A	2.4	227	96
	EA	2.4	234	
	T	2.2	214	
	EB	2.2	207	
	C	1.9	182	
4 replicate	A	4.2	211	50
	EA	2.7	135	
	T	3.1	152	
	EB	3.0	151	
	C	3.2	161	

Liquid- and gas-phase mass transfer coefficients may also be used to determine the relative importance of liquid and gas-phase resistances to mass transfer for specific chemicals and operating conditions. As shown in Equation 2-5, overall resistance to mass transfer ($1/K_L A$) may be written as the sum of liquid-phase resistance to mass transfer ($1/k_L A$) and gas-phase resistance to mass transfer ($1/k_g A \cdot H_c$). These resistances are shown graphically in Figure 7-3 for each chemical in Experiment 2. As shown in Figure 7-3, overall resistance to mass transfer for acetone and ethyl acetate is dominated by resistance in the gas phase. On the other hand, overall resistance to mass transfer for toluene, ethylbenzene, and cyclohexane is insignificant compared with their respective liquid-phase resistances to mass transfer.

7.1.4.4. Mass Closure

The ranges of mass closure for each chemical were 98% to 102% for acetone, 98% to 105% for ethyl acetate, 89% to 107% for toluene, 86% to 100% for ethylbenzene, and 82% to 103% for cyclohexane. All mass closure values are given in the Appendix.

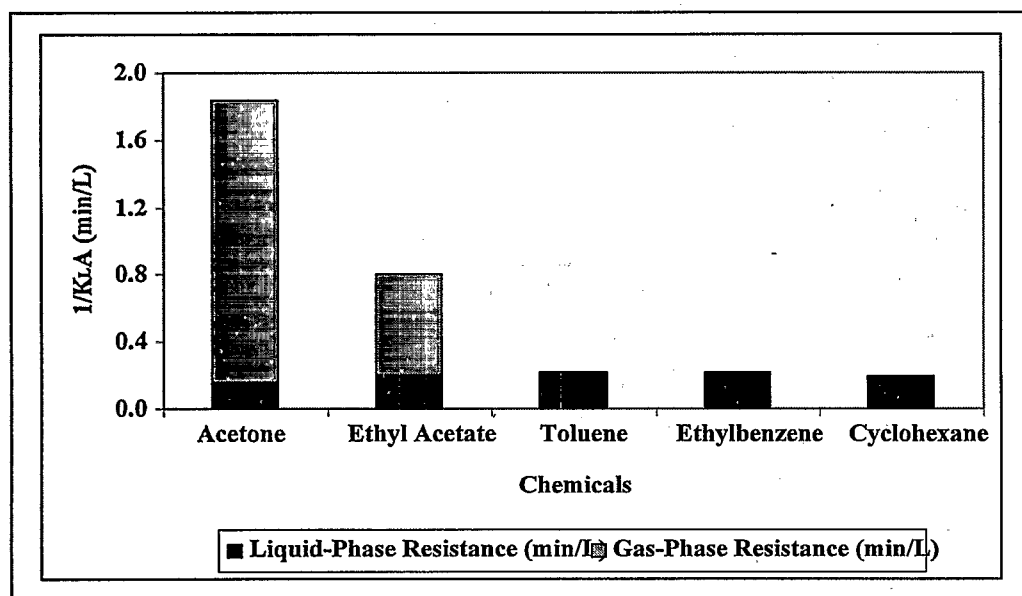


Figure 7-3. Resistances to mass transfer for each chemical in Experiment 2.

7.2. BATHTUB FILL EXPERIMENTS

7.2.1. Experimental System

As before, the same experimental system constructed for shower/bathtub flow-through experiments was used for bathtub fill experiments. However, the drain was plugged with a rubber stopper so the bathtub would fill. An additional modification shown in Figure 7-4 was a different liquid sample port location. Samples were collected from this port by pumping water from the bathtub using a 102 cm perforated 0.635 cm OD Teflon™ tube. The perforated Teflon™ tube was angled in the bathtub pool such that water was drawn through the holes at different depths, resulting in a more distributed liquid sample. Tracer reservoir samples were collected in the same manner as for shower and bathtub flow-through experiments. For bathtub fill experiments, only gas sample ports #1 and #2 were used. A more evenly distributed gas concentration was expected for these experiments.

7.2.2. Experimental Design

As with flow-through experiments, bathtub fill experimental variables were liquid temperature and liquid flowrate. Four experiments were completed with two replicates.

7.2.3. Source-Specific Methodology

No different preexperimental tasks were completed for fill experiments, except for the introduction of a drain plug.

7.2.3.1. Sample Schedule

Bathtub fill experiments varied in length depending on experimental flowrate. For experiments completed at 9.1 L/min, the bathtub was filled for 8 minutes. For experiments completed at 6.1 L/min, the bathtub was filled for 12 minutes. A total of 10 liquid-phase samples were collected for each fill experiment. Liquid-phase samples were collected every 2 minutes for the high flowrate experiments, and every 3 minutes for the low flowrate experiments. Tracer reservoir samples were collected within 90 seconds of every bathtub sample.

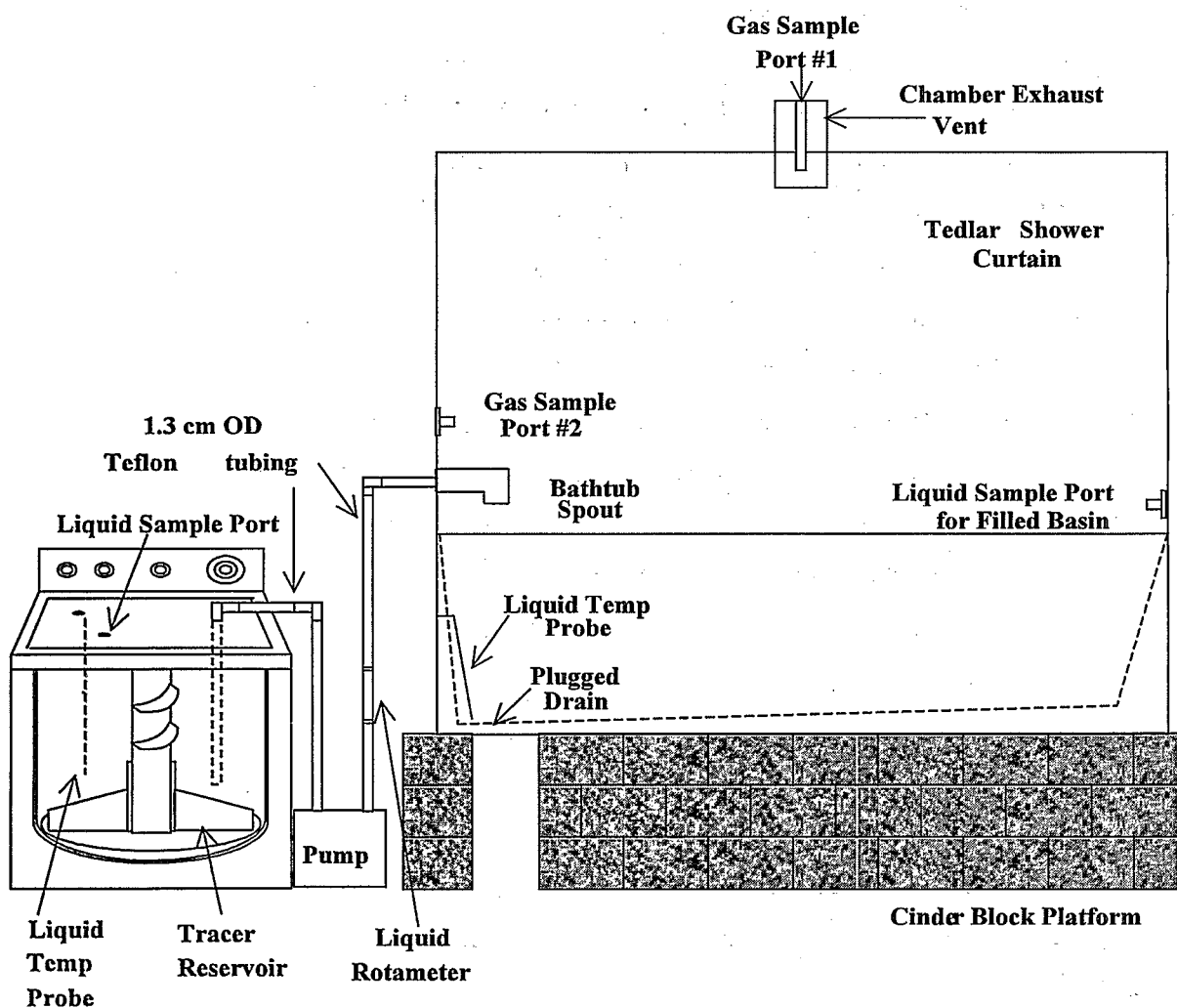


Figure 7-4. Bathtub fill experimental system.

An initial gas sample was collected from sample port #1 before starting the experiment. Once an experiment began, a single gas sample was collected at this port for the duration of the experiment, followed by a 1-minute sample collected immediately after the experiment. One-minute gas samples were also collected at sample port #2. These samples were scheduled such that a bathtub liquid sample was collected at the midpoint of the gas sample time. Six gas-phase samples were collected for each experiment.

7.2.3.2. Ventilation Rates

Prediction of bathtub (fill) ventilation rates followed the same procedure developed for showers (see Section 4.3.2).

7.2.3.3. Parameter Estimation

The same parameter estimation techniques outlined in Section 6.1.3.3 for washing machine fill cycle experiments applied to bathtub fill experiments. Stripping efficiencies and values of $K_L A$ were based on liquid-phase data for all chemicals. Values of $K_L A$ were based on gas-phase data for acetone and ethyl acetate and were based on liquid-phase data for toluene, ethylbenzene, and cyclohexane.

7.2.4. Bathtub Fill Results

Five bathtub fill experiments were completed to predict chemical mass emissions. Bathtub fill results can be combined with bathtub surface volatilization results presented in Section 7.3 to characterize total mass emissions during a typical bathing event. Ventilation rates, stripping efficiencies, and mass transfer coefficients ($K_L A$, $k_l A$, $k_g A$, and k_g/k_l) are presented in this chapter and are based on the experimental methodology presented in Sections 3.0 and 7.2.3. In addition, the effects of liquid temperature, liquid fill rate, and chemical properties are discussed. The operating conditions for each mass transfer experiment are listed in Table 7-5.

7.2.4.1. Chemical Stripping Efficiencies

Chemical stripping efficiencies (η) are reported in Table 7-6. Stripping efficiencies for high flowrate (9.1 L/min) experiments were based on a fill time of 8 minutes whereas stripping efficiencies for low flowrate (6.1 L/min) experiments were based on a fill time of 12 minutes. Liquid-phase concentrations did not change significantly in the bathtub after approximately 1 minute of fill time, thereby allowing comparison of stripping efficiencies based on different experimental times.

Table 7-5. Bathtub (fill) operating conditions

Experiment #	Liquid temperature (°C)	Fill time (min)	Liquid flowrate (L/min)	Liquid volume (L)	Gas flowrate (L/min)
1	24	8:00	9.1	73	373
2	35	8:00	9.1	73	379
2 replicate	36	8:00	9.1	73	373
3	23	12:00	6.1	73	370
4	35	11:23	6.1	69	377

Table 7-6. Chemical stripping efficiencies (η) for bathtub (fill) experiments

Expt. #	Liquid Temp.	Liquid Flowrate	Acetone η (%)	Ethyl Acetate η (%)	Toluene η (%)	Ethylbenzene η (%)	Cyclohexane η (%)
1	Cold	High	4.9	3.0	31	33	46
2	Warm	High	5.2	5.3	30	32	47
2 rep	Warm	High	2.0	3.1	31	32	46
3	Cold	Low	5.8	3.1	29	31	43
4	Warm	Low	7.7	7.0	30	29	46

Stripping efficiencies for acetone ranged from 2.0% to 7.7%, with the highest value for low flowrate and warm water. The average stripping efficiency for acetone was 5.1%. Stripping efficiencies for ethyl acetate ranged from 3.0% to 7.0%, with an overall average of 4.3%.

There was little deviation between stripping efficiencies for toluene, ethylbenzene, and cyclohexane. Average stripping efficiencies were 30% for toluene, 31% for ethylbenzene, and 46% for cyclohexane. As expected, toluene and ethylbenzene had similar results. Cyclohexane stripping efficiencies were somewhat higher for this set of bathtub experiments, indicating more influence of gas-phase resistance to mass transfer for more volatile chemicals, possibly from formation of bubbles in the underlying pool as the bathtub filled.

Experiment 2 was repeated. The relative difference between stripping efficiencies determined for Experiments 2 and 2 replicate were 88% for acetone, 52% for ethyl acetate, 3.3% for toluene, 0% for ethylbenzene, and 2.2% for cyclohexane.

7.2.4.2. K_LA Values

Values of K_LA for all chemicals and operating conditions are reported in Table 7-7, and were based on the same fill times discussed for stripping efficiencies. In general, for all chemical tracers, values of K_LA were higher at higher liquid flowrates. The average values of K_LA at a liquid flowrate of 6.1 L/min were 0.39 L/min for acetone, 0.86 L/min for ethyl acetate, 2.7 L/min for toluene, 2.6 L/min for ethylbenzene, and 4.9 L/min for cyclohexane. At a liquid flowrate of 9.1 L/min, the average values of K_LA were 0.54 L/min for acetone, 1.3 L/min for ethyl acetate, 4.4 L/min for toluene, 4.4 L/min for ethylbenzene, and 8.5 L/min for cyclohexane.

7.2.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

Values of K_LA for each chemical were separated into the components of k_LA and k_gA using Equation 2.5 and a value of k_g/k_L determined for each specific experiment. These values are reported in Table 7-8. For the bathtub filling events, values of k_g/k_L ranged from 27 to 77, with an average value of 51. Bathtub water during a filling event is characterized by splashing at the surface and entrainment of air creating visible bubbles in the pool. As such, the average k_g/k_L value for high flowrate experiments was somewhat lower (45) than the average value associated with low flowrate experiments (62). These values were similar in magnitude to values of k_g/k_L predicted for surface aerator systems (38 to 110) (Hsieh et al., 1991).

7.2.4.4. Mass Closure

For bathtub fill experiments, the percentage of mass recovered was based on Equation 3.11 applied for the entire time of fill. The range of mass closure for each chemical was 96% to 101% for acetone, 103% to 108% for ethyl acetate, 89% to 106% for toluene, 87% to 96% for ethylbenzene, and 68% to 87% for cyclohexane.

Table 7-7. Values of K_LA for bathtub (fill) experiments

Experiment #	Liquid temp.	Liquid flowrate	Acetone K_LA (L/min)	Ethyl acetate K_LA (L/min)	Toluene K_LA (L/min)	Ethylbenzene K_LA (L/min)	Cyclohexane K_LA (L/min)
1	Cold	High	0.45	1.0	4.1	4.4	7.1
2	Warm	High	0.53	1.4	5.3	5.9	11
2 rep	Warm	High	0.64	1.5	3.7	3.8	7.4
3	Cold	Low	0.39	0.71	2.6	2.7	4.4
4	Warm	Low	0.39	1.0	2.7	2.5	5.4

Table 7-8. Liquid- and gas-phase mass transfer coefficients for bathtub (fill) experiments

Experiment #	Chemical	$k_l A$ (L/min)	$k_g A$ (L/min)	k_g/k_l
1	A	7.1	395	56
	EA	4.9	274	
	T	4.4	244	
	EB	4.6	257	
	C	7.1	396	
2	A	9.3	253	27
	EA	8.3	228	
	T	5.8	159	
	EB	6.3	172	
	C	11	311	
2 replicate	A	5.9	303	51
	EA	5.3	269	
	T	3.8	193	
	EB	4.0	202	
	C	7.4	376	
3	A	4.7	365	77
	EA	2.7	208	
	T	2.7	208	
	EB	2.8	220	
	C	4.4	344	
4	A	4.2	191	46
	EA	3.8	175	
	T	2.8	129	
	EB	2.6	121	
	C	5.4	245	

7.3. SURFACE VOLATILIZATION EXPERIMENTS

7.3.1. Experimental System

The same experimental system presented in Section 7.2.1 was used for surface volatilization experiments. The only addition to the system was a simulated person. A model of a person was designed using empty 3 L Tedlar™ bags. Four bags were connected with string to create joints between each bag. Additional strings were attached to the "head" bag and "foot" bag that allowed them to be moved from outside the system. Moving the strings resulted in bag motions that created waves and moderate splashing in the bathtub pool.

7.3.2. Experimental Design

Four combinations of conditions were studied for surface volatilization experiments. Experimental variables were liquid temperature and the presence of a person.

7.3.3. Source-Specific Methodology

Surface volatilization experiments followed bathtub fill experiments, so the bathtub contained a well-mixed solution of chemical tracers. The following tasks were completed before starting the surface volatilization portion of an experiment:

- For appropriate experiments, the Tedlar™ person was placed in the bathtub pool
- An initial liquid sample was collected
- An initial gas sample was collected from port #1.

7.3.3.1. Sample Schedule

Based on typical bathing times, surface volatilization experiments lasted 20 minutes. Liquid samples were collected from the bathtub every 4 minutes. Eight liquid-phase samples were collected for each experiment. Gas samples were collected from port #2 for 2 minutes each, starting at 3, 7, 11, and 15. minutes. A single gas sample was collected for the 20-minute experiment from port #1. A final gas sample was also collected from this port. Six gas samples were collected for each experiment.

7.3.3.2. Ventilation Rates

Prediction of ventilation rates associated with bathtub surface volatilization experiments followed the same procedure developed for showers (see Section 4.3.2).

7.3.3.3. Parameter Estimation

Chemical volatilization rates for bathtub experiments with standing water (no additional motion) were nearly zero. Therefore, for surface volatilization experiments, chemical stripping efficiencies were calculated using the following equation, which included gas-phase data:

$$\eta = \frac{Q_g \int_{t_1}^{t_2} C_g \Delta t + V_g (C_{g, \text{end}} - C_{g, \text{in}})}{V_l C_{l, \text{in}}} \quad (7-1)$$

where

Q_g = system ventilation rate (L^3/T)

C_g = integrated gas sample average concentration (M/L^3)

Δt = time of experiment (T)

V_g = headspace volume (L^3)

V_l = bathtub fill volume (L^3)

$C_{g, \text{end}}$ = final gas-phase concentration in headspace (M/L^3)

$C_{g, \text{in}}$ = initial gas-phase concentration in headspace (M/L^3)

$C_{l, \text{in}}$ = average liquid-phase concentration in tracer reservoir (M/L^3).

Bathtub surface volatilization experiments with a simulated person were characterized by significantly higher chemical stripping efficiencies than were quiescent bathtub experiments, such that liquid-phase values were used.

Because of the limited chemical volatilization for quiescent conditions (no "person" present), values of $K_L A$ were not determined for this source. Values of $K_L A$ for bathtub experiments with a simulated person were determined using the methodology outlined in Section 3.6.2. Gas-phase data were used to find the best-fit value of $K_L A$ for acetone and ethyl acetate, and liquid-phase data were used to find the best-fit value of $K_L A$ for toluene, ethylbenzene, and cyclohexane.

7.3.4. Bathtub Surface Volatilization Results

Six bathtub surface volatilization mass transfer experiments were completed. Surface volatilization results may be combined with bathtub fill results presented in Section 7.2.4 to characterize total mass emissions during typical bathing events. Based on the experimental methodology presented in Sections 3.0 and 7.3.3, the ventilation rates, overall chemical stripping efficiencies, and mass transfer coefficients ($K_L A$, $k_l A$, $k_g A$, and k_g/k_l) are presented in this

chapter. In addition, effects of liquid temperature, presence of a person, and chemical properties on each response are discussed.

Operating conditions for each mass transfer experiment are given in Table 7-9.

7.3.4.1. Chemical Stripping Efficiencies

Stripping efficiencies for each chemical are reported in Table 7-10. As mentioned in Section 7.3.3.3, chemical stripping efficiencies for experiments not using a simulated person (Experiments 1, 1 replicate, and 2) were based on gas-phase data. Values reported in Table 7-10 for these experiments ranged from 0.57% to 15% for all chemicals.

There were significant reductions in liquid-phase chemical concentrations for Experiments 3 through 4 replicate, allowing stripping efficiencies to be determined based on differences in liquid concentration. Stripping efficiencies ranged from 1.6% to 7.3% for acetone, 3.4% to 9.8% for ethyl acetate, 27% to 32% for toluene, 26% to 32% for ethylbenzene, and 30% to 41% for cyclohexane. The degree of splashing associated with surface volatilization experiments with a simulated person could not be reasonably quantified and was not consistent. As a result, it is difficult to report more than just stripping efficiency values for these experiments; that is, neither a trend analysis nor a determination of relative difference in values was completed.

Table 7-9. Bathtub surface volatilization operating conditions

Experiment #	Liquid temperature (°C)	Person present?	Liquid volume (L)	Gas flowrate (L/min)
1	23	No	73	370
1 replicate	24	No	73	377
2	34	No	69	377
3	24	Yes	73	373
4	33	Yes	73	379
4 replicate	35	Yes	73	373

Table 7-10. Chemical stripping efficiencies (η) for bathtub surface volatilization experiments

Experiment #	Liquid temp.	Person present ?	Acetone η (%)	Ethyl acetate η (%)	Toluene η (%)	Ethylbenzene η (%)	Cyclohexane η (%)
1	Cold	No	0.57	1.6	7.9	5.1	4.7
1 rep	Cold	No	2.5	5.9	13	7.6	13
2	Warm	No	2.7	6.4	14	8.3	15
3	Cold	Yes	1.6	3.4	32	32	39
4	Warm	Yes	4.5	9.8	27	26	41
4 rep	Warm	Yes	7.3	8.9	30	29	30

7.3.4.2 K_LA Values

Values of K_LA were not determined for experiments using still water (no person present) given the near zero rate of chemical volatilization. Values of K_LA were determined, however, for Experiments 3, 4, and 4 replicate and are reported in Table 7-11.

Values of K_LA for each chemical were 0.11 to 0.25 L/minute for acetone, 0.24 to 0.49 L/minute for ethyl acetate, 1.2 L/minute for toluene, 1.1 to 1.2 L/minute for ethylbenzene, and 1.2 to 2.0 L/minute for cyclohexane. Again, because of the inconsistent nature of these experiments, values of K_LA are merely indicators of the order of magnitude of chemical volatilization during bathing events.

A representative experimental plot for surface volatilization experiments with a simulated person is presented in Figure 7-5. The plot shows toluene data. Experimental conditions were warm water and presence of the simulated person. The resulting value of K_LA for toluene for this example was 1.2 L/min.

Table 7-11. Values of K_LA for bathtub surface volatilization experiments

Experiment #	Liquid temp.	Person present?	Acetone K_LA (L/min)	Ethyl acetate K_LA (L/min)	Toluene K_LA (L/min)	Ethylbenzene K_LA (L/min)	Cyclohexane K_LA (L/min)
3	Cold	Yes	0.11	0.24	1.2	1.2	1.4
4	Warm	Yes	0.25	0.49	1.2	1.1	2.0
4 rep	Warm	Yes	0.23	0.40	1.2	1.1	1.2

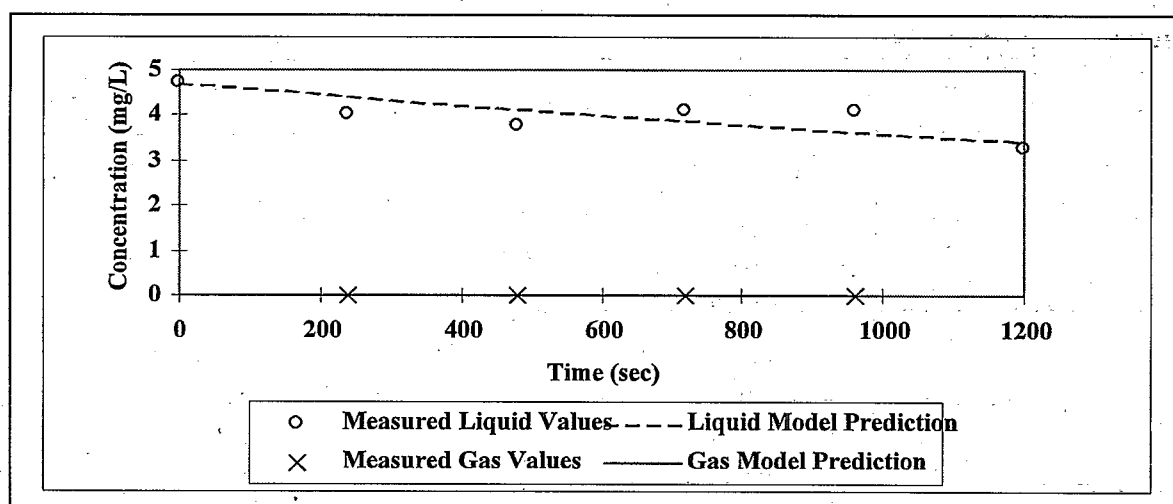


Figure 7-5. Toluene experimental data for Experiment 4 replicate.

7.3.4.3. Liquid- and Gas-Phase Mass Transfer Coefficients

Values of $K_L A$ for each chemical were separated into the components of $k_l A$ and $k_g A$ using Equation 2.5 and a value of k_g/k_l determined for each specific experiment (see Sections 3.6.3 and 3.6.4 for methodology). Values of $k_l A$ and $k_g A$ are reported in Table 7-12 for each chemical in addition to values of k_g/k_l for Experiments 3, 4, and 4 replicate.

For bathtub surface volatilization experiments with a simulated person present, values of k_g/k_l ranged from 54 to 78. Despite the randomness associated with these experiments, values of k_g/k_l were relatively similar in magnitude.

7.3.4.4. Mass Closure

For bathtub surface volatilization experiments, the percentage of mass recovered was based on Equation 3.10. The range of mass closure for surface volatilization experiments with no person present was 99% to 104% for acetone, 100% to 105% for ethyl acetate, 96% to 110% for toluene, 86% to 100% for ethylbenzene, and 93% to 117% for cyclohexane. For surface volatilization experiments involving a simulated person, the range of mass closure was 98% to 103% for acetone, 104% to 109% for ethyl acetate, 90% to 100% for toluene, 83% to 92% for ethylbenzene, and 80% to 91% for cyclohexane.

Table 7-12. Liquid- and gas-phase mass transfer coefficients for bathtub surface volatilization experiments

Experiment #	Chemical	$k_l A$ (L/min)	$k_g A$ (L/min)	k_g/k_l
3	A	1.8	97	54
	EA	1.2	63	
	T	1.3	69	
	EB	1.3	68	
	C	1.4	76	
4	A	1.8	143	78
	EA	1.4	107	
	T	1.2	97	
	EB	1.1	88	
	C	2.0	156	
4 replicate	A	1.6	122	78
	EA	1.1	84	
	T	1.2	97	
	EB	1.1	88	
	C	1.2	94	

8. MODEL APPLICATIONS

All experimental results reported herein as well as previously reported research results have been compiled into a database that is provided in the Appendix. Each entry in the database summarizes a particular experiment, including operating conditions, chemical stripping efficiencies, and, where applicable, estimated values of $K_L A$, $k_1 A$, $k_g A$, and percent mass recovery. The database could serve as a tool for a user to find the most appropriate modeling parameters for a specific contamination event. At this time, the database includes 164 shower results (including 50 from this study), 44 dishwasher results (all from this study), 128 washing machine results (including 114 from this study), 85 bathtub results (all from this study), and 33 kitchen sink results. Using the available information, it is now possible to estimate chemical emissions from tap water sources for numerous scenarios, without having to assume 100% volatilization for all chemicals.

Based on experimental results, values of $K_L A$ and, where appropriate, headspace ventilation rates can be used in conjunction with associated source mass balance models to determine chemical emissions during a specific source event. In this chapter, an example event for each of the four sources discussed herein is presented. The methodology for predicting emissions for other chemicals of interest is provided. For each source, toluene was used as the surrogate compound (chemical j in Equation 2-15). Dibromochloromethane (DBCM), a common disinfection by-product, and methyl ethyl ketone (MEK), a common solvent, were used as the chemicals of interest (chemical i in Equation 2-15). A comparison of these three chemicals is provided in Table 8-1. For all cases, chemicals were assumed to be present in the water supply at a concentration of 10 $\mu\text{g/L}$.

8.1. SHOWER MODEL APPLICATION

Mass balance Equations 2-28 and 2-30 may be used to predict chemical liquid- and gas-phase concentrations during a shower event of any duration. The associated mass emissions may be estimated during a shower event by applying the predicted liquid-phase concentrations to Equation 2-32. For this example, a shower duration of 10 minutes was chosen. Other operating

Table 8-1. Comparison of the three chemicals used in model applications

Chemical	$H_c @ 25^\circ\text{C}$ ($\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$) ^a	$D_l @ 24^\circ\text{C}$ (cm^2/sec) ^b	$D_g @ 24^\circ\text{C}$ (cm^2/sec) ^b
Toluene	0.27	9.1×10^{-6}	0.085
Dibromochloromethane	0.048	1.0×10^{-5}	0.086
Methyl Ethyl Ketone	0.0060	9.8×10^{-6}	0.097

^aFrom Ashworth et al., 1988.

^bFrom Tucker and Nelken, 1990.

conditions for this example, based on experimental operating conditions, were a water temperature of 35°C, a liquid flowrate of 9.1 L/minute, and a ventilation rate of 379 L/minute (resulting in an air exchange rate of 13/hour). A coarse water spray was assumed. The value of $K_L A$ for toluene (used in Equations 2-28 and 2-30 to predict toluene liquid- and gas-phase concentrations, respectively, associated with these operating conditions) was assumed to be 12 L/minute. This value is the average $K_L A$ determined for shower Experiments 5, 6, and 6 replicate (see Section 4.4.2). It should be noted that several values of $K_L A$ based on different shower operating conditions are available in the experimental database (Appendix).

Based on an inlet liquid-phase concentration of 0.010 mg/L and an initial gas-phase concentration of 0 mg/L, the predicted mass emission rate for toluene is presented in Figure 8-1.

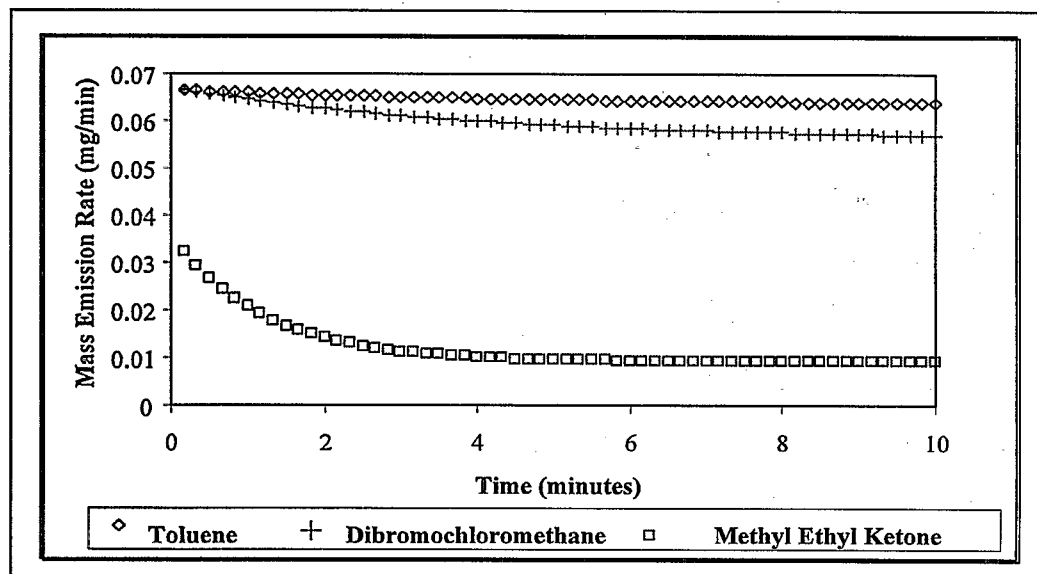


Figure 8-1. Mass emission rates for three chemicals for example shower event.

The total mass of emitted toluene was calculated by integrating under the mass emission rate curve shown in Figure 8-1. For this example, the total emitted mass of toluene was 650 μg . The total mass that entered the system was 910 μg . Thus, the overall stripping efficiency for toluene during the 10-minute shower event was 71%. The peak gas-phase concentration within the shower stall occurred at 10 minutes and was approximately 150 $\mu\text{g}/\text{m}^3$.

The mass emission rates for DBCM and MEK, two chemicals not used in this study, are also shown in Figure 8-1. For toluene and DBCM, the mass emission rate slowly decreased with time as each chemical accumulated within the shower stall. This effect was more dramatic for MEK, the chemical with the lower Henry's law constant. The overall stripping efficiencies for DBCM and MEK were 66% and 13%, respectively.

The procedure for predicting mass emissions for any chemical of interest based on the results of this study is illustrated by means of a step-by-step method for one chemical of interest, MEK. The shower conditions described earlier for toluene also apply for this example.

Step 1: Choose an experimental tracer to be the surrogate compound with an associated value of $K_L A$.

For this example, toluene was chosen as the surrogate compound (chemical j). As shown earlier, the value of $K_L A$ for toluene and associated operating conditions was 12 L/minute.

Step 2: Choose appropriate experimentally determined k_g/k_l value for source operating conditions.

The value of k_g/k_l for any shower event was estimated to be 160 (see Section 4.4.3).

Step 3: Estimate Ψ_i for surrogate compound (chemical j) and chemical of interest (chemical i).

For toluene and MEK, the value of Ψ_i was calculated using Equation 2-12 as:

$$\Psi_i = \left(\frac{D_{l,MEK}}{D_{l,toluene}} \right)^{\frac{2}{3}} = 1.1$$

Step 4: Estimate Ψ_g for surrogate compound (chemical j) and chemical of interest (chemical i).

For toluene and MEK, the value of Ψ_g was calculated using Equation 2-13 as:

$$\Psi_g = \left(\frac{D_{g,MEK}}{D_{g,toluene}} \right)^{\frac{2}{3}} = 1.1$$

Step 5: Estimate Ψ_m for surrogate compound (chemical j) and chemical of interest (chemical i).

Ψ_m was calculated using Equation 2-15 with values from Steps 2 through 4 and Henry's law constants for each chemical listed in Table 8-1. The values of Henry's law constant for each chemical were adjusted for a temperature of 35°C using correlations developed by Ashworth et al. (1988).

$$\Psi_m = \Psi_i \Psi_g \left\{ \frac{H_{ci}}{H_{cj}} \right\} \left\{ \frac{1 + \left[\frac{k_{gj}}{k_{lj}} \right] H_{cj}}{\Psi_i + \Psi_g H_{ci} \left[\frac{k_{gj}}{k_{lj}} \right]} \right\}$$

$$\Psi_m = (1.1) \cdot (1.1) \cdot \left\{ \frac{0.0033}{0.37} \right\} \cdot \left\{ \frac{1 + 160 \cdot 0.37}{1.1 + 1.1 \cdot 0.0033 \cdot 160} \right\} = 0.38.$$

Step 6: Calculate $K_L A$ for chemical of interest.

The value of $K_L A$ for MEK may be estimated using:

$$K_L A_{\text{MEK}} = \Psi_m \cdot K_L A_{\text{toluene}} = 0.38 \cdot 12 \text{ L/minute} = 4.5 \text{ L/minute.}$$

Step 7: Predict liquid- and gas-phase concentrations as a function of time.

Applying a value of $K_L A$ of 4.5 L/minute to Equations 2-28 and 2-30 enables prediction of liquid- and gas-phase concentrations, respectively, of MEK. At 10 minutes, the gas-phase concentration in the shower stall is the following:

$$C_{g,10\text{min}} = \frac{B}{D} + \left(C_{g,0} - \frac{B}{D} \right) \exp(-Dt)$$

$$C_{g,10\text{min}} = \frac{2.0 \times 10^{-5} \text{ mg}/(\text{min} \cdot \text{L})}{0.83/\text{min}} + \left(0 - \frac{2.0 \times 10^{-5} \text{ mg}/(\text{min} \cdot \text{L})}{0.83/\text{min}} \right) \exp(-0.83/\text{min} \cdot 10 \text{ min}) = 2.4 \times 10^{-5} \text{ mg/L}$$

where

$$B = \frac{\left(Q_l C_{l,\text{in}} \left(1 - \exp\left(-\frac{K_L A}{Q_l}\right) \right) \right) + Q_g C_{g,\text{in}}}{V_g}$$

$$B = \frac{9.1 \text{ L/min} \cdot 0.01 \text{ mg/L} \cdot \left(1 - \exp\left(-\frac{4.5 \text{ L/min}}{9.1 \text{ L/min}}\right) \right) + 379 \text{ L/min} \cdot 0 \text{ mg/L}}{1745 \text{ L}} = 2.0 \times 10^{-5} \text{ mg}/(\text{min} \cdot \text{L})$$

$$D = \frac{\left(\left(\frac{Q_l}{H_c} \right) \left(1 - \exp \left(- \frac{K_L A}{Q_l} \right) \right) + Q_g \right)}{V_g}$$

$$D = \frac{\left(\left(\frac{9.1 \text{ L/min}}{0.0033} \right) \left(1 - \exp \left(- \frac{4.5 \text{ L/min}}{9.1 \text{ L/min}} \right) \right) + 379 \text{ L/min} \right)}{1745 \text{ L}} = 0.83 \text{ min}^{-1}$$

The resulting liquid-phase concentration at the shower drain at 10 minutes is as follows:

$$C_{l,\text{out}} = C_{l,\text{in}} \exp \left(- \frac{K_L A}{Q_l} \right) + \left(\frac{C_g}{H_c} \right) \left(1 - \exp \left(- \frac{K_L A}{Q_l} \right) \right)$$

$$C_{l,\text{out}} = 0.01 \text{ mg/L} \cdot \exp \left(- \frac{4.5 \text{ L/min}}{9.1 \text{ L/min}} \right) + \left(\frac{2.4 \times 10^{-5} \text{ mg/L}}{0.0033} \right) \left(1 - \exp \left(- \frac{4.5 \text{ L/min}}{9.1 \text{ L/min}} \right) \right) = 0.0090 \text{ mg/L}$$

Step 8: Calculate mass emission rate as a function of time.

The mass emission rate for MEK at 10 minutes is calculated using Equation 2-32:

$$E_{10\text{min}} = Q_l (C_{l,\text{in}} - C_{l,\text{out},10\text{min}}) = 9.1 \text{ L/minute} \cdot (0.01 \text{ mg/L} - 0.0090 \text{ mg/L}) = 0.0091 \text{ mg/min.}$$

The resulting mass emission rate as a function of time is shown in Figure 8-1. The lower value of $K_L A$ for MEK resulted in a significantly lower mass emission rate. The same eight-step procedure was applied for toluene and DBCM, which resulted in a $K_L A$ value of 12 L/minute for DBCM. The mass emission rate for DBCM is slightly lower than the rate for toluene in that DBCM has a lower Henry's law constant than toluene.

In previous modeling exercises, it has been assumed that the overall mass transfer coefficients between two chemicals may be solely related by $\Psi_i = K_{Li}/K_{Lj}$. This relationship requires only knowledge of liquid molecular diffusion coefficients for each compound in accordance with Equation 2.12, and is valid when gas-phase resistance to mass transfer is negligible for each compound. As discussed previously, an assumption that gas-phase resistance is negligible is often reasonable only when both compounds are highly volatile (e.g., cyclohexane and radon). Equation 2.15, used to predict Ψ_m , incorporates a chemical's liquid- and gas-phase resistance to mass transfer and will converge to Ψ_i as k_g/k_l and/or H_c for both i and j become relatively large. Thus, Ψ_m is a more appropriate value to predict values of K_LA for chemicals of wide-ranging volatility.

However, in the case of showers, the value of k_g/k_l is sufficiently large that the value of K_LA for even chemicals as low in volatility as MEK may be estimated using Ψ_i . As a result, the more important variable to predict is the chemical's Henry's law constant, which affects the concentration driving force for mass transfer (Equation 2.28) and hence mass emission rates. For this example, the emitted mass of DBCM was approximately 600 μg , and the emitted mass of MEK was approximately 120 μg .

8.2. DISHWASHER MODEL APPLICATION

Mass balance Equations 2-23 and 2-24 may be used to predict chemical emissions during a dishwasher event of single or multiple cycles, that is, number of separate fills during operation. For this example, the following dishwasher event was assumed: a prerinse cycle of 3.5 minutes, a wash cycle of 10 minutes, and two rinse cycles of 6 and 14 minutes, respectively. Each cycle was followed by a 2-minute drain period. The cycle order and times were based on those for the experiment dishwasher. Other specific operating conditions included a water temperature of 55°C and a liquid fill volume of 7.4 L resulting in a headspace volume of 181 L. Based on experiment results, the headspace ventilation rate was assumed to be 5.7 L/minute. The value of K_LA for toluene (used in Equations 2-23 and 2-24 to predict liquid and gas-phase concentrations associated with these operating conditions) was assumed to be 35 L/minute (average of K_LA values determined for Experiments 5 through 8 replicate in Table 5-5) for all cycles. Because of the relatively small difference in values of K_LA between experiments of different operating conditions

(wash versus rinse), the value of $K_L A$ chosen for toluene represented the average of all dishwasher results for heated water experiments (see Section 5.4.3).

The mass emission rate for toluene was predicted using the following steps:

Step 1: Predict liquid- and gas-phase concentrations as a function of time.

The liquid-phase concentration in the dishwasher water after 3.5 minutes of operation for the first cycle (prerinse cycle) is predicted using Equation 2-23:

$$C_1 = C_{1,0} \left[\exp\left(-\frac{D}{2}t\right) \cosh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) + \left(\frac{BF}{Z} + \frac{EC_{1,0}}{Z} - \frac{DC_{1,0}}{2}\right) \left[\frac{1}{\sqrt{\frac{D^2}{4} - E}} \exp\left(-\frac{D}{2}t\right) \sinh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) \right] \right]$$

$$\begin{aligned} C_1 &= 0.01 \text{ mg/L} \left[\exp\left(-\frac{5.0/\text{min}}{2} 3.5 \text{ min}\right) \cosh\left(\left(\sqrt{\frac{(5.0/\text{min})^2}{4} - 0.15/\text{min}}\right) 3.5 \text{ min}\right) \right] \\ &+ \left(\frac{7.5/\text{min} \cdot 1.9 \times 10^{-3} \text{ mg/(L/min)}}{4.7/\text{min}} + \frac{0.15/\text{min} \cdot 0.01 \text{ mg/L}}{4.7/\text{min}} - \frac{5.0/\text{min} \cdot 0.01 \text{ mg/L}}{2} \right) \\ &\cdot \left[\frac{1}{\sqrt{\frac{(5.0/\text{min})^2}{4} - 0.15/\text{min}}} \exp\left(-\frac{5.0/\text{min}}{2} 3.5 \text{ min}\right) \sinh\left(\left(\sqrt{\frac{(5.0/\text{min})^2}{4} - 0.15/\text{min}}\right) 3.5 \text{ min}\right) \right] \end{aligned}$$

$$= 5.6 \times 10^{-4} \text{ mg/L.}$$

where

$$D = Z + Y = 4.7/\text{min} + 0.34/\text{min} = 5.0/\text{min}$$

$$Z = \frac{K_L A}{V_l} = \frac{35 \text{ L/min}}{7.4 \text{ L}} = 4.7 / \text{min}$$

$$Y = \frac{Q_g}{V_g} + \frac{K_L A}{V_g H_c} = \frac{5.7 \text{ L/min}}{18 \text{ L}} + \frac{35 \text{ L/min}}{18 \text{ L} \cdot 0.63} = 0.34 / \text{min}$$

$$E = ZY - BX = 4.7 / \text{min} \cdot 0.34 / \text{min} - 7.5 / \text{min} \cdot 0.19 / \text{min} = 0.15 / \text{min}$$

$$B = \frac{K_L A}{V_l H_c} = \frac{35 \text{ L/min}}{7.4 \text{ L} \cdot 0.63} = 7.5 / \text{min}$$

$$X = \frac{K_L A}{V_g} = \frac{35 \text{ L/min}}{18 \text{ L}} = 0.19 / \text{min}$$

$$F = ZC_{g,0} + XC_{l,0} = 4.7 / \text{min} \cdot 0 + 0.19 / \text{min} \cdot 0.01 \text{ mg/L} = 0.0019 \text{ mg/(L} \cdot \text{min)}$$

The gas-phase concentration at the end of the first cycle is calculated using Equation 2-24:

$$C_g = C_{g,0} \exp\left(-\frac{D}{2}t\right) \cosh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) + \left(F - \frac{DC_{g,0}}{2}\right) \left[\frac{1}{\sqrt{\frac{D^2}{4} - E}} \exp\left(-\frac{D}{2}t\right) \sinh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) \right]$$

$$C_g = 0 \text{ mg/L} \exp\left(-\frac{5.1 / \text{min}}{2} \cdot 3.5 \text{ min}\right) \cosh\left(\left(\sqrt{\frac{(5.1 / \text{min})^2}{4} - 0.15}\right) 3.5 \text{ min}\right)$$

$$+ \left(1.9 \times 10^{-3} \text{ mg/(L} \cdot \text{min)} - \frac{5.1 / \text{min} \cdot 0 \text{ mg/L}}{2}\right) \left[\frac{1}{\sqrt{\frac{(5.1 / \text{min})^2}{4} - 0.15}} \exp\left(-\frac{5.1}{2} \cdot 3.5 \text{ min}\right) \sinh\left(\left(\sqrt{\frac{(5.1 / \text{min})^2}{4} - 0.15 / \text{min}}\right) 3.5 \text{ min}\right) \right]$$

$$= 3.5 \times 10^{-4} \text{ mg/L.}$$

Step 2: Calculate the mass emission rate as a function of time.

Using Equation 2-31, the mass emission rate at the end of the first cycle is

$$E = Q_g C_{g,3.5\text{min}} = 5.7 \text{ L/minute} \bullet 3.5 \times 10^{-4} \text{ mg/L} = 0.0020 \text{ mg/min.}$$

Step 3: Predict ventilation decay rate during drain period.

Between each cycle was a drain period, where water used during the cycle was pumped from the machine. During the drain period, the gas phase was modeled using the following equation with a ventilation rate of 5.7 L/minute:

$$C_g = C_{g,0} \exp\left(-\frac{Q_g}{V_g} t\right) \quad (8-1)$$

where

C_g = headspace concentration (M/L³)

$C_{g,0}$ = headspace concentration at end of cycle (M/L³)

Q_g = machine ventilation rate (L³/T)

V_g = machine headspace volume (L³)

t = time (T).

The concentration of toluene in the dishwasher headspace at the end of the 2 minute drain period is:

$$C_g = 3.5 \times 10^{-4} \text{ mg/L} \bullet \exp\left(-\frac{5.7 \text{ L/min}}{181 \text{ L}} \bullet 2 \text{ min}\right) = 3.3 \times 10^{-4} \text{ mg/L.}$$

Step 4: Repeat Steps 1 to 3 for number of dishwasher cycles.

Each cycle was modeled separately with an inlet liquid-phase concentration of 10 µg/L. However, the gas-phase concentration of each cycle was dependent on that of the previous cycle; that is, the initial gas-phase concentration for each cycle ($C_{g,0}$) was equal to the final gas-phase concentration of the previous drain cycle.

The total mass of emitted toluene was calculated by integrating under the mass emission rate curve shown in Figure 8-2. For this example, the total mass of toluene emitted over the entire cycle was predicted to be 157 μg . It should be noted that an additional 117 μg of residual toluene was retained in the dishwasher headspace at the end of the final rinse cycle. This residual would be released as a "puff" if the dishwasher were opened soon after the final cycle. This more concentrated release might contribute a greater exposure route than corresponding emissions during the actual dishwasher operation. The stripping efficiency for toluene over all dishwasher cycles was 93%.

By means of the first six steps outlined in Section 8.1, values of $K_L A$ for DBCM and MEK were estimated. Although values of $K_L A$ were less important for this source because of equilibrium limitations, a value of $K_L A$ for each chemical was needed to properly use the mass balance model. As discussed in Section 5.4.4, a value of k_g/k_l for dishwashers was not determined. Thus, to predict a value of $K_L A$ for a chemical of interest, a k_g/k_l ratio had to be assumed. Given the hydrodynamic similarity between dishwashers and showers, the k_g/k_l value of 160 determined for showers was used. The value of $K_L A$ estimated for DBCM was 37 L/minute, resulting in an

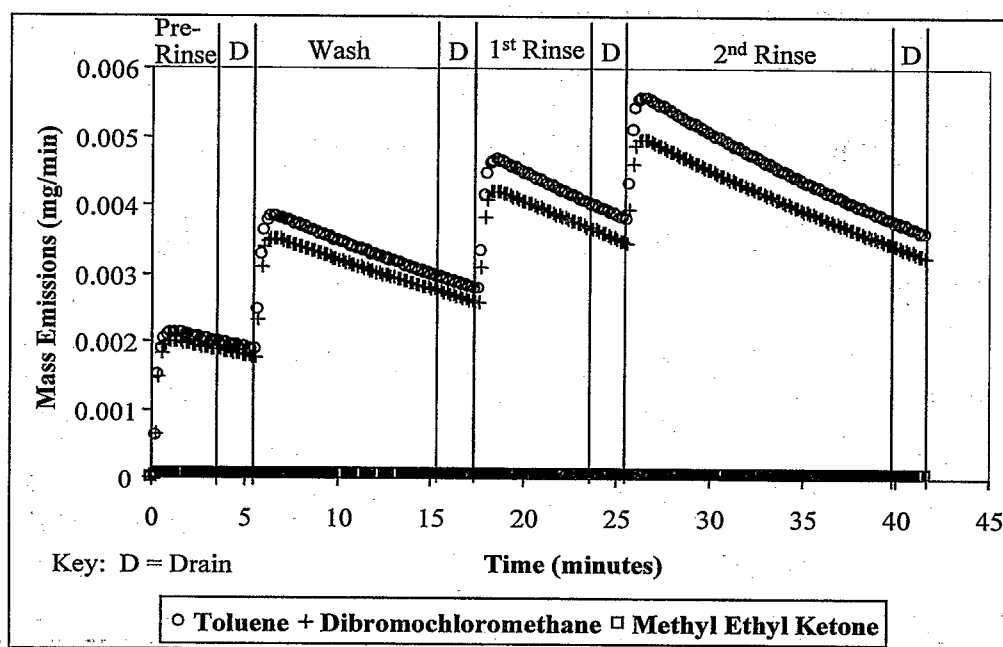


Figure 8-2. Mass emission rates for three chemicals for example dishwasher event.

overall emitted mass of 143 μg , and stripping efficiency of 84%. As for toluene, a potential puff release mass was calculated for DBCM to be 107 μg . The value of $K_L A$ for MEK for this example was estimated to be 5.7 L/minute, resulting in a total mass emitted of 2.5 μg , a puff release of 1.9 μg , and a stripping efficiency of 1.5%. Using the identical operating conditions listed for toluene and an inlet concentration of 10 $\mu\text{g/L}$ yielded mass emission rates for each chemical as presented in Figure 8-2. Again, the lower values of $K_L A$ and Henry's law constant for MEK resulted in a significantly lower mass emission rate. To better see the shape of MEK emissions over time, the ordinate of Figure 8-2 was magnified as shown in Figure 8-3.

The general shape of the mass emission rate curve reflected the approach to a dynamic equilibrium condition for each chemical. Although DBCM had a slightly greater value of $K_L A$ than toluene, the mass emission rate for DBCM was lower because of equilibrium limitations in the headspace. Thus, for equilibrium-limited cases, the value of $K_L A$ for a given chemical merely indicates how rapidly equilibrium will be achieved within the headspace. As a result of the insignificance of $K_L A$, more emphasis is placed on the accuracy of a chemical's Henry's law

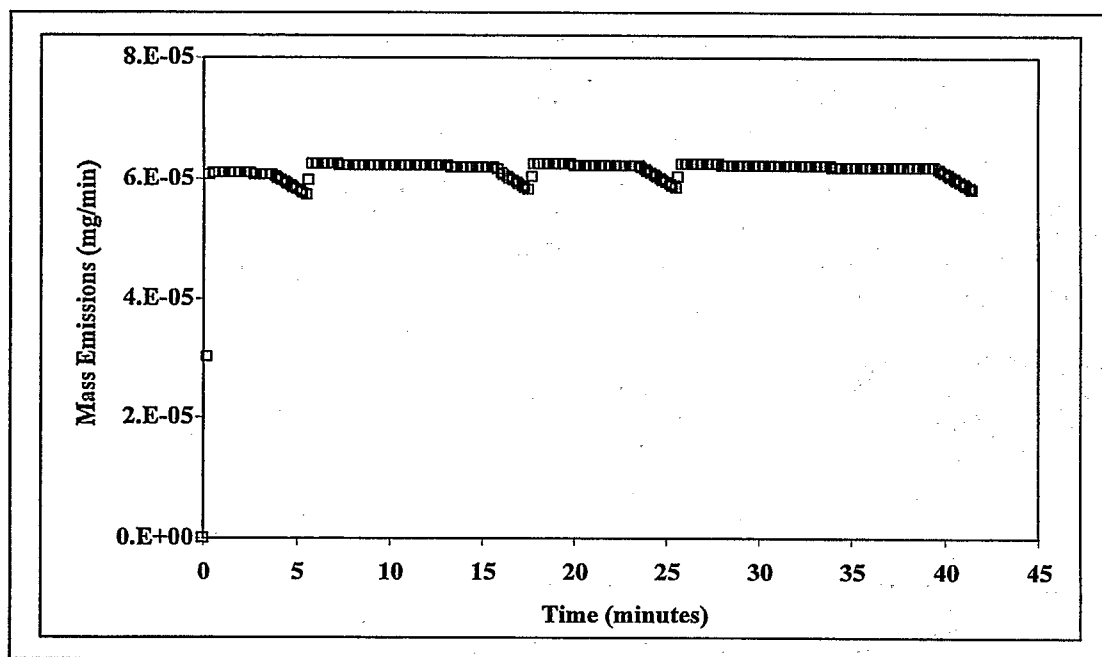


Figure 8-3. Amplification of Figure 8-2 to show MEK mass emission rate.

constant. Currently, there is a lack of information regarding Henry's law constants for potential drinking water contaminants, especially at higher temperatures.

8.3. WASHING MACHINE MODEL APPLICATION

Different mass balance equations were used to predict emissions from each washing machine cycle. Mass balance Equations 3-8 and 3-9 were used to predict chemical concentrations during the fill cycle of a washing machine event. Mass balance Equations 2-23 and 2-24 were used to predict chemical concentrations during the wash and rinse cycles of a washing machine event. Similar to dishwashers, each cycle was modeled separately, with the initial conditions reflecting previous cycles. For example, the initial liquid- and gas-phase concentrations for the wash cycle were equal to the final liquid- and gas-phase concentrations, respectively, for the first fill cycle. Both fill cycles had an identical inlet chemical liquid-phase concentration of $10 \mu\text{g/L}$. As for dishwashers, the headspace concentration during the drain/spin period for a washing machine was modeled using Equation 8-1 and the emission rate was calculated using Equation 2-31.

For this example, a washing machine event was assumed to consist of a 3.3-minute fill cycle at a flowrate of 13.8 L/minute ($\approx 46 \text{ L}$ total liquid volume), a 10-minute wash cycle, a 4-minute drain and spin cycle, another 3.3-minute fill cycle also at a flowrate of 13.8 L/minute , a 4-minute rinse cycle, and finally a 6-minute drain and spin cycle. Other specific operating conditions for this example were a water temperature of 21°C , and ventilation rates of 55 L/minute for the fill cycle, and 53 L/minute for the remaining cycles. With a fill volume of 46 L and an approximate equivalent clothing volume of 11 L , the headspace volume was 92 L .

To predict mass emissions associated with the example operating conditions, a value of $K_L A$ for toluene was chosen for each cycle. An "average" value of $K_L A$ was not used for all cycles because of the significant effects of operating conditions on $K_L A$ observed for washing machine experiments. Values of $K_L A$ for toluene were as follows: 2.9 L/minute for both fill cycles, 0.58 L/minute for the wash cycle, and 0.84 L/minute for the rinse cycle. On the basis of these values of $K_L A$ and an inlet concentration of $10 \mu\text{g/L}$, the mass emission rate was calculated using the following steps:

Step 1: Predict liquid- and gas-phase concentrations as a function of time for fill cycle.

A second-order Runge-Kutta solution technique was used to determine the liquid- and gas-phase concentrations during filling. The applicable general second-order solution technique is:

$$x^{n+1} = x^n + \frac{\Delta t}{2} \{f(t^n, x^n) + f[t^n + \Delta t, x^n + f(t^n, x^n)]\} \quad (8-2)$$

Applying this method to Equations 2-25 and 2-26 and using 1-second time steps enabled prediction of the liquid- and gas-phase concentrations at each time step, respectively.

The liquid-phase concentration in the washing machine water after filling for 3.3 minutes follows:

Find first-order solution:

$$x^{n+1} = \left[\frac{Q_l C_{l,in}}{V_l^n} - \frac{Q_l C_l^n}{V_l^n} - \frac{K_L A C_l^n}{V_l^n} + \frac{K_L A C_g^n}{V_l^n H_c} \right] \cdot \Delta t + C_l^n$$

$$x^{n+1} = \left[\frac{13.8 \text{ L/min} \cdot 0.01 \text{ mg/L}}{45.8 \text{ L}} - \frac{13.8 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{45.8 \text{ L}} - \frac{2.9 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{45.8 \text{ L}} + \frac{2.9 \text{ L/min} \cdot 3.5 \times 10^{-4} \text{ mg/L}}{45.8 \text{ L} \cdot 0.24} \right] \cdot (1/60 \text{ min} + 0.0084 \text{ mg/L})$$

Find $f(t^n, x^n)$:

$$f(t^n, x^n) = \left[\frac{Q_l C_{l,in}}{V_l^n} - \frac{Q_l C_l^n}{V_l^n} - \frac{K_L A C_l^n}{V_l^n} + \frac{K_L A C_g^n}{V_l^n H_c} \right]$$

$$f(t^n, x^n) = \frac{13.8 \text{ L/min} \cdot 0.01 \text{ mg/L}}{45.8 \text{ L}} - \frac{13.8 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{45.8 \text{ L}} \\ - \frac{2.9 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{45.8 \text{ L}} + \frac{2.9 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{45.8 \text{ L} \cdot 0.24} = 3.0 \times 10^{-5} \text{ mg/(L} \cdot \text{min)}$$

Find $f[t^n + \Delta t, x^n + \Delta t f(t^n, x^n)]$:

$$f(t^n + \Delta t, x^n + \Delta t f(t^n, x^n)) = \left[\frac{Q_1 C_{1,\text{in}}}{V_1^{n+1}} - \frac{Q_1 C_1^{n+1}}{V_1^{n+1}} - \frac{K_L A C_1^{n+1}}{V_1^{n+1}} + \frac{K_L A C_g^n}{V_1^{n+1} H_c} \right]$$

$$f(t^n + \Delta t, x^n + \Delta t f(t^n, x^n)) = \frac{13.8 \text{ L/min} \cdot 0.01 \text{ mg/L}}{46 \text{ L}} - \frac{13.8 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{46 \text{ L}}$$

$$- \frac{2.9 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{46 \text{ L}} + \frac{2.9 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{46 \text{ L} \cdot 0.24} = 3.0 \times 10^{-5} \text{ mg/(L} \cdot \text{min)}$$

Insert appropriate values into Equation 8-2:

$$C_1^{n+1} = 0.0084 \text{ mg/L} + \frac{1/6.0 \text{ min}}{2} \cdot (3.1 \times 10^{-5} \text{ mg/L} \cdot \text{min} + 3.0 \times 10^{-5} \text{ mg/L} \cdot \text{min}) = 0.0084 \text{ mg/L}$$

Note: The second-order solution is virtually equivalent to the first-order solution; thus, a fourth-order solution technique was not deemed necessary. Also, values used in this example were rounded. More exact values were used in spreadsheet calculations.

Similarly, the gas-phase concentration in the washing machine headspace at the end of filling is calculated as follows:

Find first-order solution:

$$C_g^{n+1} = \left[\frac{-Q_g C_g^n}{(V_t - V_1^n)} + \frac{Q_1 C_g^n}{(V_t - V_1^n)} + \frac{K_L A C_1^n}{(V_t - V_1^n)} - \frac{K_L A C_g^n}{(V_t - V_1^n) H_c} \right] \Delta t + C_g^n$$

$$C_g^{n+1} = \left[\frac{-55 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L})} + \frac{13.8 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L})} + \frac{2.9 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L})} - \frac{2.9 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L}) \cdot 0.24} \right]$$

$$\cdot (1/60 \text{ min}) + 3.4 \times 10^{-4} \text{ mg/L} = 3.5 \times 10^{-5} \text{ mg/L}$$

Find $f(t^n, x^n)$:

$$f(t^n, x^n) = \left[\frac{-Q_g C_g^n}{(V_t - V_1^n)} + \frac{Q_1 C_g^n}{(V_t - V_1^n)} + \frac{K_L A C_1^n}{(V_t - V_1^n)} - \frac{K_L A C_g^n}{(V_t - V_1^n) H_c} \right]$$

$$f(t^n, x^n) = \frac{-55 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L})} + \frac{13.8 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L})} \\ + \frac{2.9 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L})} - \frac{2.9 \text{ L/min} \cdot 3.4 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 45.8 \text{ L}) \cdot 0.24}$$

Find $f[t^n + \Delta t, x^n + \Delta t f(t^n, x^n)]$:

$$f(t^n + \Delta t, x^n + \Delta t f(t^n, x^n)) = \left[\frac{-Q_g C_g^{n+1}}{(V_t - V_1^{n+1})} + \frac{Q_1 C_g^{n+1}}{(V_t - V_1^{n+1})} + \frac{K_L A C_1^n}{(V_t - V_1^{n+1})} - \frac{K_L A C_g^{n+1}}{(V_t - V_1^{n+1}) H_c} \right]$$

$$f(t^n + \Delta t, x^n + \Delta t f(t^n, x^n)) = \frac{-55 \text{ L/min} \cdot 3.5 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 46 \text{ L})} + \frac{13.8 \text{ L/min} \cdot 3.5 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 46 \text{ L})} \\ + \frac{2.9 \text{ L/min} \cdot 0.0084 \text{ mg/L}}{(150 \text{ L} - 46 \text{ L})} - \frac{2.9 \text{ L/min} \cdot 3.5 \times 10^{-4} \text{ mg/L}}{(150 \text{ L} - 46 \text{ L}) \cdot 0.24}$$

Insert appropriate values into Equation 8-2:

$$C_g^{n+1} = 3.5 \times 10^{-4} \text{ mg/L} + \left(\frac{1/60 \text{ min}}{2} \right) (5.6 \times 10^{-5} \text{ mg/L} \cdot \text{min} + 5.6 \times 10^{-5} \text{ mg/L} \cdot \text{min})$$

Step 2: Calculate mass emission rate for each time step during fill cycle.

Through use of Equation 2-31, the mass emission rate at the end of the fill cycle is:

$$E = Q_g C_{g,3.4\text{min}} = 55 \text{ L/minute} \cdot 3.5 \times 10^{-4} \text{ mg/L} = 0.019 \text{ mg/min.}$$

Step 3: Predict liquid- and gas-phase concentrations as a function of time during wash cycle.

Equations 2-23 and 2-24 were used to predict liquid- and gas-phase concentrations as a function of time. Refer to dishwasher steps for use of equations. The initial liquid-phase concentration is equal to the final fill liquid-phase concentration, which in this example is 0.0084 mg/L. Likewise, the initial gas-phase concentration is equal to the final fill gas-phase concentration, which in this example is 3.5×10^{-4} mg/L. At the end of the 10-minute wash cycle, the estimated liquid-phase concentration is 0.0075 mg/L and the estimated gas-phase concentration is 8.1×10^{-5} mg/L.

Step 4: Calculate mass emission rate as a function of time for wash cycle.

Again, with the use of Equation 2-31, the mass emission rate may be calculated. For this example, the rate is:

$$E = 53 \text{ L/minute} \cdot 8.1 \times 10^{-5} \text{ mg/L} = 0.0043 \text{ mg/min.}$$

Step 5: Predict ventilation decay rate during drain period.

Between the end of the wash cycle and the next fill is a drain period, where water used during the wash cycle is pumped from the washing machine. This drain/spin cycle was

modeled using Equation 8.1 with a ventilation rate of 53 L/minute. The concentration of toluene in the washing machine headspace at the end of the 4-minute drain period is nearly zero.

Step 6: Repeat Steps 1 through 5 for rinse fill, rinse, and final drain.

The wash and rinse cycles were modeled separately, both with an inlet liquid-phase concentration of 10 µg/L.

The total mass emitted for the entire washing machine event was 210 µg. The mass emission rate is shown in Figure 8-4. The mass of toluene remaining in the headspace after the final spin cycle was 0.41 µg, significantly lower than the residual mass observed in the dishwasher headspace. The low residual washing machine headspace mass may be attributed to its relatively high ventilation rate, which effectively flushes the headspace of the machine. The stripping efficiency integrated over all cycles for toluene was 22%.

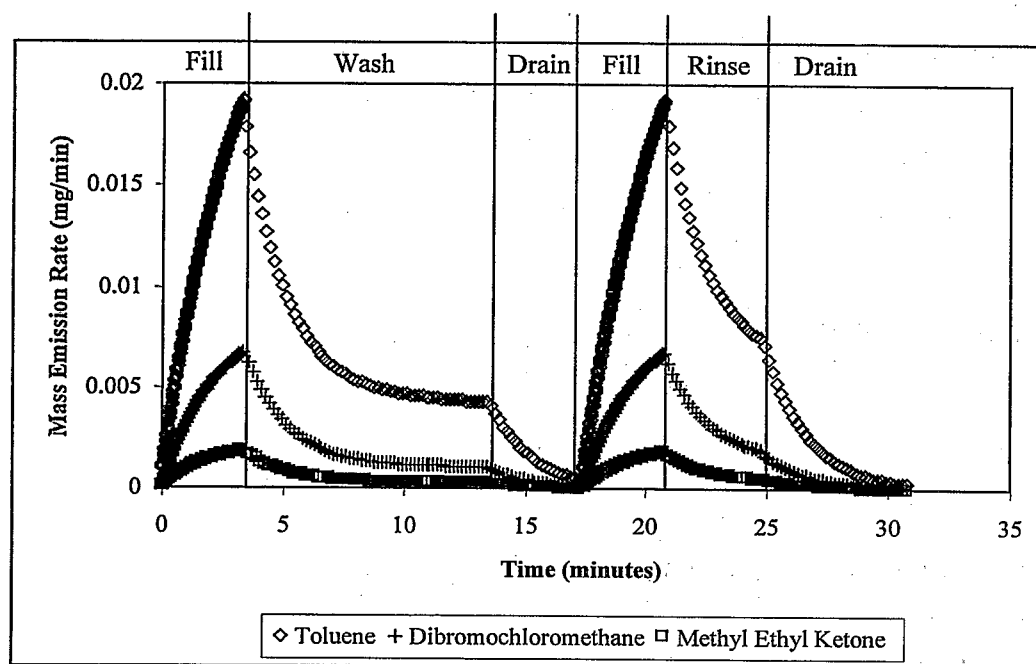


Figure 8-4. Mass emission rates for three chemicals for example washing machine event.

In addition to having different values of $K_L A$, each type of cycle was characterized by a different k_g/k_l ratio. The k_g/k_l values chosen for this example were 9.5 for the fill cycles and 2.2 for the wash and rinse cycles. The resulting values of $K_L A$ for DBCM using the six-step procedure described in Section 8.1 were 1.1 L/minute for the fill cycles, 0.12 L/minute for the wash cycle, and 0.18 L/minute for the rinse cycle. The resulting values of $K_L A$ for MEK following the same procedure were 0.31 L/minute for the fill cycle, 0.030 L/minute for the wash cycle, and 0.044 L/minute for the rinse cycle.

To illustrate the importance of gas-phase resistance to mass transfer, the total mass emissions for DBCM and MEK were calculated using values of $K_L A$ based on Ψ_m and values of $K_L A$ based only on Ψ_l . The total mass emitted for DBCM using Ψ_m to predict $K_L A$ was 67 μg (stripping efficiency of 7.1%) compared with 150 μg emitted when Ψ_l was used to predict $K_L A$. The total mass emitted for MEK using Ψ_m to predict $K_L A$ was 18 μg (stripping efficiency of 1.9%) compared with 65 μg emitted when Ψ_l was used to predict $K_L A$.

8.4. BATHTUB MODEL APPLICATION

The same mass balance equations used for modeling emissions from washing machines were used for bathtubs (see washing machine steps). Equations 3.8 and 3.9 were used to predict chemical concentrations in the liquid and gas phases, respectively, during the fill portion of bathtub use. Equations 2.23 and 2.24 were used to predict liquid- and gas-phase concentrations during the bathing portion of bathtub use. Equation 2.33 was used to predict resulting mass emissions. The inlet chemical concentration was 10 $\mu\text{g/L}$. The initial concentrations for the bathing portion were equal to the final liquid- and gas-phase concentrations for the fill portion. For this example, a bathtub was assumed to be filled for 8 minutes using a water flowrate of 9.1 L/minute, resulting in a total liquid volume of approximately 73 L. There was a 20-minute bathing period after the filling experiment. It was also assumed that the bathing event occurred in a 13 m^3 bathroom with an air exchange rate of 1.0/hour ($Q_g = 217 \text{ L/minute}$). The temperature of the water was equivalent to the warmest experimental temperature of 36°C and remained constant for the entire bathing event.

The values of $K_L A$ chosen for toluene were based on bathtub fill and surface volatilization experiments, respectively. Given the narrow range of bathtub fill results, an average value of 4.4 L/minute was chosen based on high flowrate average. Similarly, an average value of 1.2 L/minute was chosen to represent surface volatilization with a person present. The resulting mass emissions for the entire bathtub event are plotted in Figure 8-5. Integrating under the mass emission rate curve, the total mass of toluene emitted was 375 μg , with a corresponding integrated stripping efficiency of 51%.

As with the previous sources, values of $K_L A$ were predicted for DBCM and MEK. For a bathtub event, the k_g/k_l ratio associated with filling was chosen to be 51 and the k_g/k_l ratio associated with bathing was chosen to be 70. The values of $K_L A$ estimated for DBCM using Ψ_m were 4.0 L/minute for filling the tub and 1.1 L/minute for surface volatilization. The values of $K_L A$ estimated for MEK using Ψ_m were 0.72 L/minute for filling the tub and 0.25 L/minute for surface volatilization. The mass emission rates for these two chemicals are presented in Figure 8-5.

The total mass emitted of DBCM using Ψ_m to predict $K_L A$ was 350 μg (stripping efficiency of 48%) compared with 380 μg emitted using Ψ_l to predict $K_L A$. The total mass emitted of MEK using Ψ_m to predict $K_L A$ was 89 μg (stripping efficiency of 12%) compared with 250 μg emitted using Ψ_l to predict $K_L A$.

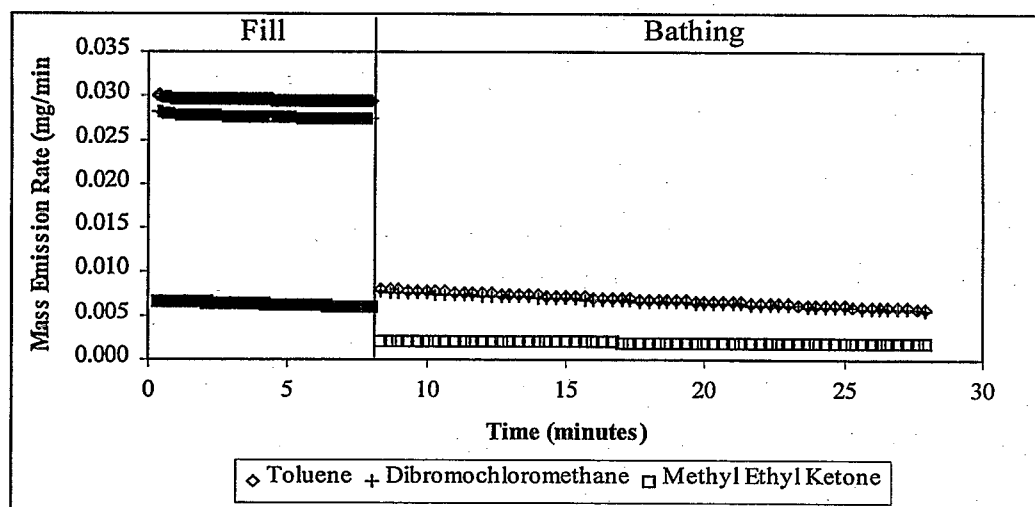


Figure 8-5. Mass emission rates for three chemicals for example bathtub event.

9. SUMMARY AND CONCLUSIONS

9.1. SUMMARY

The research described in this report consisted of 113 experiments involving 5 tracer chemicals (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane) and 4 sources (showers, dishwashers, washing machines, and bathtubs). The source experiments completed for this study have significantly increased the existing knowledge base of published experiments involving chemical volatilization from drinking water to indoor air.

A determined attempt was made to follow a rigorous quality assurance project plan and to perform mass closure assessments on all sources. The latter are not often reported in the published literature and necessitate simultaneous collection of liquid and gas samples. The resulting database allowed determination of chemical stripping efficiencies (η), overall mass transfer coefficients ($K_L A$), and liquid- and gas-phase mass transfer coefficients ($k_l A$ and $k_g A$) for each chemical and source. In addition, headspace ventilation rates were measured for washing machines and dishwashers.

An important contribution from these experiments was the calculation of mass transfer parameters for acetone and ethyl acetate, two chemicals with Henry's law constants considerably lower than any used in previous experiments. Use of these lower volatility chemicals greatly improves the ability to estimate mass transfer coefficients for many disinfection by-products, pesticides, and other low-volatility compounds.

The ratio of gas- and liquid-phase mass transfer coefficients (k_g/k_l) was calculated for varying operating conditions for each source. As described in Chapter 2 and illustrated in Chapter 8 of this report, knowledge of the magnitude of k_g/k_l is critical for improved estimates of chemical volatilization from drinking water to indoor air. This is particularly true when an overall mass transfer coefficient for one chemical is to be extrapolated to a second chemical of interest. Experimentally predicted values of k_g/k_l should serve as a major contribution of this study.

A series of dynamic emission models were developed for each source and were based on fundamental reactor analyses, mass balances, and mass transfer kinetics. The experimental mass transfer coefficients, air exchange rates, and protocols described in this report can be used as direct input values or to estimate reasonable input values for the reported emission models. In addition to input parameters based on this research, values based on previous research are provided. All experimental results related to chemical volatilization from tap water are now available in a single database provided in the Appendix. The database contains 454 experimental results (including 293 results from this study) and is a valuable source of information for those interested in modeling human inhalation exposures related to specific contamination scenarios.

Values of $K_L A$, $k_g A$, $k_l A$, k_g/k_l , and headspace ventilation rates are presented in Chapters 4 through 7. A summary of chemical stripping efficiencies is provided in Table 9-1 for each source. The ranges of stripping efficiencies for each chemical and source reflect the fact that, for some sources, the rate of volatilization from drinking water to indoor air, and subsequent human exposure, is highly dependent on source operating conditions. In many cases, assuming 100% volatilization will significantly overestimate emissions and human inhalation exposure to chemicals originating in drinking water.

A set of general conclusions is provided in Section 9.2. Source-specific conclusions are provided in Sections 9.3 through 9.6. Finally, recommendations for future research are provided in Section 9.7.

Table 9-1. Summary of experimental stripping efficiencies and k_g/k_l

Chemical	Showers	Bathtubs ^a	Dishwashers	Washing machines ^b
Acetone	6.3 – 16	2.6 – 14	18 – 55	3.8 – 38
Ethyl Acetate	15 – 36	4.6 – 16	*	*
Toluene	61 – 77	35 – 53	96 – 98	30 – 99
Ethylbenzene	62 – 75	33 – 54	97 – 98	31 – 99
Cyclohexane	65 – 80	64 – 69	100	40 – 100
k_g/k_l	110 – 223	Flow-through: 37 – 96 Fill: 27 – 77 Bathing: 54 – 78	*	Fill: 4.5 – 20 Wash/Rinse: 0.13 – 8.6

^aStripping efficiency based on combined effects of filling and bathing (20 minutes) in series.

^bStripping efficiency based on combined effects of fill and wash (or rinse) in series.

*Unable to determine

9.2. CONCLUSIONS: GENERAL

The findings of this study lead to several general conclusions about all, or most, sources and chemicals:

1. System operating conditions can have a significant effect on chemical emissions. This is particularly true for lower volatility chemicals (e.g., ethyl acetate and acetone) and for all chemicals emitted from washing machines.
2. For higher volatility chemicals (e.g., with Henry's law constants greater than toluene), chemical stripping efficiencies should vary by approximately 30% or less (relative) over a wide range of system operating conditions for showers, bathtubs, and dishwashers.
3. Although many operating conditions can affect chemical volatilization rates from water to indoor air, water temperature appears to have the greatest effect over all sources and chemicals. This is generally caused by a combination of increases in Henry's law constants (H_c) and liquid-phase mass transfer coefficients, as well as by increases in headspace ventilation rates for washing machines and dishwashers.
4. Chemical stripping efficiencies increase as Henry's law constant increases from lower volatility chemicals, (e.g., acetone and ethyl acetate) to higher volatility chemicals (e.g., toluene, ethylbenzene, and cyclohexane). However, stripping efficiencies are relatively insensitive to Henry's law constant for H_c greater than that of toluene. The one exception is for the fill cycle of bathtubs.
5. Failure to properly account for gas-phase resistance to mass transfer can lead to significant overestimates of chemical volatilization to indoor air. This is particularly true for lower volatility chemicals or those sources with low values of gas- to liquid-phase mass transfer coefficients (k_g/k_l) (e.g., washing machines).

6. Significant improvements in emissions estimates are possible by incorporating appropriate values of k_g/k_l into the estimation process. However, values of k_g/k_l are specific to individual systems and operating conditions and should therefore be chosen carefully.
7. The use of dual tracers with similar physicochemical properties (e.g., toluene and ethylbenzene) can be effective as internal checks of the quality of experimental results.

9.3. CONCLUSIONS: SHOWERS

Showers are the most extensively studied source of chemical volatilization from drinking water to indoor air. However, previous studies are limited in terms of the separation of gas- and liquid-phase mass transfer coefficients, and analyses of compounds with significant gas-phase resistance to mass transfer. Furthermore, previous researchers have speculated on the validity of the assumptions that shower stall atmospheres are well mixed. The following conclusions stem from this study and directly address the issues listed above:

1. The shower stall atmosphere is relatively well mixed; that is, gas-phase concentrations should be relatively homogenous throughout a shower stall.
2. Gas-phase resistance to mass transfer dominates the overall resistance to mass transfer for acetone and chemicals with Henry's law constants lower than H_c for acetone. Gas- and liquid-phase resistances are both important for compounds with H_c similar to ethyl acetate.
3. Liquid-phase resistance to mass transfer is dominant for chemicals with H_c greater than toluene. Thus, overall mass transfer coefficients for two or more of these compounds can be related using only liquid-phase molecular diffusion coefficients.
4. On the basis of the results of this study, stripping efficiencies for chemicals with H_c greater than or equal to toluene should range from 60% to 80%. Slight deviations between this

range and those previously reported by other researchers are likely caused by differences in showerheads.

5. Mass emission rates from water to shower stall air decrease with time depending on the volatility of a chemical and its approach to equilibrium. Thus, knowing a chemical's Henry's law constant at typical shower temperatures is important.

9.4. CONCLUSIONS: DISHWASHERS

Previous to this study, dishwashers had received little attention as emission sources. The following conclusions are derived from 29 experiments involving a commercial dishwasher:

1. Dishwashers are characterized by a low, but continuous and constant, headspace ventilation rate during operation.
2. Dishwashers are extremely effective at stripping a wide range of chemicals from water.
3. High stripping efficiencies (approaching 100% for chemicals with $H_c \geq$ toluene) can be attributed to the high water temperatures used in dishwashers, relatively high liquid-phase mass transfer coefficients associated with airborne droplets, and large headspace volume relative to water volume within the dishwasher.
4. Chemicals are rapidly stripped from water to the interior headspace of dishwashers during the first minute of water spraying, that is, during rinse and wash cycles. Thereafter, chemicals with Henry's law constants less than or equal to those associated with ethylbenzene approach a state of chemical equilibrium.
5. The most significant release of chemicals to indoor air would occur if the dishwasher door is opened immediately after use.

9.5. CONCLUSIONS: WASHING MACHINES

Chemical emissions from washing machines have received some attention in the published literature. However, variations in machine operating conditions and chemical properties have been limited. Furthermore, previous researchers have not addressed the potential for emissions during fill cycles. The following conclusions come from 57 experiments using a commercial washing machine:

1. Washing machines are well ventilated, with air exchange rates exceeding those for dishwashers by one to two orders of magnitude.
2. The use of hot water leads to significant increases in washing machine ventilation rates caused by buoyancy-induced air flows.
3. Stripping efficiencies from washing machines, more than any other source, are extremely sensitive to system operating conditions.
4. Under appropriate conditions (hot water, rinse cycle with no detergent present, low clothes loading), stripping efficiencies for chemicals with Henry's law constants greater than toluene can approach 100%.
5. Chemical emissions during machine filling are generally lower than emissions during wash and rinse cycles.
6. During wash and rinse cycles, gas-phase resistance to mass transfer is important for all chemicals with Henry's law constants less than or equal to H_c for ethylbenzene.

9.6. CONCLUSIONS: BATHTUBS

Previous research has focused on volatilization of chemicals during shower events. The argument for such studies is that, unlike other sources, showers lead to potentially significant

human exposure. However, this is also true for bathing, that is, volatilization from bathtubs to indoor air. For this study, 17 experiments were completed to assess chemical volatilization during the filling of bathtubs, during bathing events, and for applications in which water enters a tub and is allowed to flow directly into an open drain. Significant conclusions are listed below:

1. Chemical stripping efficiencies are similar during flow-through, filling, and bathing events. Here, bathing refers to volatilization from the water surface with mild agitation of the water over a 20-minute event.
2. Stripping efficiencies are more sensitive to chemical properties, particularly Henry's law constant (H_c), during tub filling than during flow-through or surface volatilization events. This is because of the significant degree of air entrainment that occurs as the water jet impacts the underlying bath pool. Diffused air bubbles promote gas-liquid mass transfer, that is, chemicals transferred from liquid to bubbles. This transfer mechanism is sensitive to H_c , as accumulation of chemical mass in bubbles can lead to an approach to chemical equilibrium for compounds with low H_c . Furthermore, gas-phase resistance to mass transfer tends to be more significant when air bubbles are present. This fact is consistent with the relatively low value of k_g/k_l for fill events.
3. Combined stripping efficiencies for fill and bathing events are slightly lower, but comparable, to those associated with shower events. Not included in the bathtub estimate are emissions from water flowing through the tub when attempting to attain a water temperature appropriate for bathing.
4. Because of the longer exposure times, chemical emissions during the use of bathtubs may be as, or more, significant than during showers, in terms of human inhalation. This is particularly important given that small children are typically washed in bathtubs rather than showers and are generally more sensitive to chemical exposure than are healthy adults.

9.7. RECOMMENDATIONS FOR FUTURE RESEARCH

The research described herein has increased the existing knowledge base associated with chemical volatilization from water to indoor air. A natural progression would be to use the results of this study to complete an integrated exposure assessment for various water contaminants and water usage scenarios. The assessment should include bounds that account for uncertainties in mass transfer parameters and other relevant exposure factors. However, based solely on the findings of the study described in this report, recommendations for future research are as follows:

1. The database that now exists for volatilization during showers is large. Additional research related to chemical volatilization during showers is not recommended. However, information regarding aerosol formation and the associated impact on chemical volatilization for showers and other relevant sources is warranted.
2. Currently, there is a lack of information on Henry's law constants at elevated temperatures for most potential drinking water contaminants. As shown by this work, the total mass emissions from several sources are highly dependent on this parameter and could be significantly over- or underestimated for these chemicals. Additional research is needed to determine Henry's law constants at water temperatures ranging from 30°C to 60°C.
3. The results of this study suggest that volatilization during the use of bathtubs may be as, or more, significant than during showers in terms of human exposure, particularly for small children. Additional research may be warranted to improve estimates of chemical volatilization from bathtubs, including an assessment of the effects of soap films on retardation of mass transfer. Furthermore, additional studies should be completed to better simulate the kinetic energy imparted on bath water by human bathing activities.
4. The database that has been generated for dishwashers is novel and suggests that chemical equilibrium is achieved rapidly between the water and the dishwasher headspace. As such,

the rate of air exchange between dishwasher and room atmospheres is a critical parameter. In this study, that rate was quantified for a commonly purchased commercial dishwasher. It would be beneficial to repeat a series of air exchange experiments on several commercially available dishwashers. These experiments could be used to quantify a range or distribution of air exchange rates.

5. Washing machines may need the greatest amount of additional research based on the range of experimental results achieved for a single washing machine, and the potential for nearly complete volatilization of many chemicals. Specific research should focus on improved estimates of headspace air exchange rates, particularly during the use of hot water, and the formation of chlorination by-products during the use of sodium-hypochlorite containing bleaches. The latter was not studied as part of this research effort, but was previously documented by the principal investigator of this project. Additional washing machine designs should be considered, including upright machines (vertical door) such as are often used in laundromats.
6. Several additional sources of chemical volatilization from water to indoor air were not studied during this research effort and are deserving of future experimental work. These include toilets, indoor saunas and tubs, aquariums, and humidifiers. The latter should include centralized humidification systems, which are now common in many parts of the United States.
7. It would be beneficial to incorporate the source models developed herein into an indoor air quality model.
8. The model described in Recommendation 7 should be used in conjunction with information related to water usage and human activity patterns to assess the significance of human inhalation exposure to chemicals that originate in drinking water. An important example

involves lower volatility disinfection by-products, which should be characterized by significant gas-phase resistance to mass transfer.

9. The database and models developed during this research effort should be supported with field data. In addition to water and air sampling in a home with a contaminated water supply, other potential sources include laundromats, gymnasium shower facilities, and restaurant kitchens.

10. REFERENCES

- Ashworth, RA; Howe, GB; Mullins, ME; Rogers, TN. (1988) Air-water partitioning coefficients of organics in dilute aqueous solutions. *J Haz Mat* 18:25-36.
- Bernhardt, G; Hess, CT. (1995) Acute exposure from radon-222 and aerosols in drinking water. Written communication. Unpublished master's thesis. University of Maine.
- Box, GEP; Bisgaard, S. (1988) Statistical tools for improving designs. *Mech Eng* 110:32-40.
- Corsi, RL; Howard, C; Strader, R. (1996) Volatilization rates from water to indoor air: phase I report. Project report submitted to U.S. Environmental Protection Agency.
- Danckwerts, PV. (1951) Significance of liquid film coefficients in gas absorption. *Ind Eng Chem* 43(6):1460-1467.
- Dobbins, WE. (1956) Mechanism of gas absorption by turbulent liquids. In: *Advances in water pollution research* 2. Eckenfelder, WW, ed. New York: Pergamon Press, Ltd., pp. 61-96.
- Enviromega. (1993) Collection system organic release algorithm: user's manual. p. 13.
- Gesell, TF; Prichard, HM. (1980) The contribution of radon in tap water to indoor radon concentrations. In: *Natural radiation environment III*, Vol. 2. Houston: Technical Information Center, U.S. Department of Energy, pp. 1347-1363.
- Giardino, NJ; Andelman, JB. (1991) Poster paper presented at Annual Conference of the American Water Works Association, Philadelphia, PA.
- Giardino, NJ; Andelman, JB. (1996) Characterization of the emissions of trichloroethylene, chloroform, and 1,2-dibromo-3-chloropropane in a full-size, experimental shower. *J Exposure Anal Environ Epidemiol* 6(4):413-423.
- Giardino, NJ; Hageman, JP. (1996) Pilot study of radon volatilization from showers with implications for dose. *Environ Sci Technol* 30(4):1242-1244.
- Giardino, NJ; Andelman, JB; Borrazzo, JE; Davidson, CI. (1988) Sulfur hexafluoride as a surrogate for volatilization of organics from indoor water uses. *J Air Pollut Control Assoc* 38(3):278-280.

- Giardino, NJ; Esmen, NA; Andelman, JB. (1992) Modeling volatilization of trichloroethylene from a domestic shower spray: the role of drop-size distribution. *Environ Sci Technol* 26:1602-1606.
- Hess, CT, Weiffenbach, CV; Norton, SA. (1982) Variations of airborne and waterborne Rn-222 in houses in Maine. *Environ Int* 8:59-66.
- Higbie, R. (1935) The rate of exposure of a pure gas into a still liquid during short periods of exposure. *Trans Am Inst Chem Eng* 31:365-388.
- Hodgson, AT; Garbesi, K; Sextro, RG; Daisey, JM. (1988) Evaluation of soil-gas transport of organic chemicals into residential buildings: final report. Lawrence Berkeley Laboratory Report, contract no. DE-AC03-76SF00098.
- Hopke, PK; Raunemaa, T; Datye, V; Kuuspallo, K; Jensen, B. (1995) Assessment of exposure to radon and its decay products from showering in radon-laden water. In: *Indoor air: an integrated approach*. Morawska, L; Bofinger, ND; Maroni, N, eds. Oxford: Elsevier Science Ltd., pp. 107-110.
- Howard, CL. (1998) Volatilization rates of chemicals from drinking water to indoor air. Ph.D. dissertation, The University of Texas at Austin.
- Howard, PH, ed. (1989) *Handbook of environmental fate and exposure data for organic chemicals (vol. I)*. Boca Raton, FL: CRC Press, Inc.
- Howard, PH, ed. (1990) *Handbook of environmental fate and exposure data for organic chemicals (vol. II)*. Chelsea, MI: Lewis Publishers.
- Howard-Reed, C; Corsi, RL; Moya, J. (1999) Mass transfer of volatile organic compounds from drinking water to indoor air: the role of residential dishwashers. *Environ Sci Technol* 33:2266-2272.
- Howard, C; Corsi, RL. (1996) Volatilization of chemicals from drinking water to indoor air: role of the kitchen sink. *J Air Waste Manage Assoc* 46:830-837.
- Howard, C; Corsi, RL. (1998) Volatilization of chemicals from drinking water to indoor air: the role of residential washing machines. *J Air Waste Manage Assoc* 48:907.
- Hsieh, CC; Ro, KS; Stenstrom, MK. (1991) Estimating stripping rates and gas/liquid mass transfer coefficients of semi-volatile organic compounds in surface aeration. *Proceedings of the 64th annual WPCF conference*; Toronto, Ontario.

- Hsieh, CC; Babcock, RW, Jr.; Stenstrom, MK. (1994) Estimating semi-volatile organic compound emission rates and oxygen transfer coefficients in diffused aeration. *Water Environ Res* 66(3):206-210.
- Jo, WK; Weisel, CP; Lioy, PJ. (1990) Routes of chloroform exposure and body burden from showering with chlorinated tap water. *Risk Anal* 10(4):575-580.
- Keating, GA; McKone, TE. (1993) Measurements and evaluation of the water-to-air transfer and air concentration for trichloroethylene in a shower chamber. In: *Modeling of indoor air quality and exposure*, ASTM STP 1205. Nagda, NL, ed. Philadelphia: American Society of Testing and Materials, pp. 14-24.
- Keating, GA; McKone, TE; Gillet, JW. (1997) Measured and estimated air concentrations of chloroform in showers: effects of water temperature and aerosols. *Atmos Environ* 31(2):123-130.
- Lewis, WK; Whitman, WG. (1924) *Ind Eng Chem* 16:1215-1220.
- Lide, DR, ed. (1995) *CRC handbook of chemistry and physics* (76th ed.) Boca Raton, FL: CRC Press.
- Little, JC. (1992) Applying the two-resistance theory to contaminant volatilization in showers. *Environ Sci Technol* 26(7):1341-1349.
- Mackay, D; Shiu, WY; Sutherland, RP. (1979). Determination of air-water Henry's law constants for hydrophobic pollutants. *Environ Sci Technol* 13(9):333-337.
- Matter-Muller, C; Gujer, W; Giger, W. (1981) Transfer of volatile substances from water to the atmosphere. *Water Res* 15:1271-1279.
- McKone, TE. (1987) Human exposure to volatile organic compounds in household tap water: the inhalation pathway. *Environ Sci Technol* 21:1194-1201.
- McKone, TE; Knezovich, JP. (1991) The transfer of trichloroethylene (TCE) from a shower to indoor air: experimental measurements and their implications. *J Air Waste Manage Assoc* 41:832-837.
- Moya, J; Howard-Reed, C; Corsi, RL. (1999) Volatilization of chemicals from tap water to indoor air from contaminated water used for showering. *Environ Sci Technol* 33:2321-2327.

- Munz, C; Roberts, PV. (1989) Gas- and liquid-phase mass transfer resistances of organic compounds during mechanical surface aeration. *Water Res* 23(5):589-601.
- Partridge, JE; Horton, TR; Sensintaffer, EL. (1979) A study of ^{222}Rn released from water during typical household activities. Office of Radiation Programs, Eastern Environmental Radiation Facility, Technical Note ORP/EERF-79-1. Montgomery, AL: U.S. EPA.
- Roberts, PV; Dandliker, P; Matter-Muller, C. (1984) Volatilization of organic pollutants in wastewater treatment model studies (EPA/600/2-84-047). Cincinnati: U.S. Environmental Protection Agency.
- Schoene, K; Steinhanses, J. (1985) Determination of Henry's law constant by automated head space-gas chromatography. *Fresenius Z Anal Chem* 321:538-543.
- Shepherd, J; Kemp, J; Corsi, RL. (1996) Chloroform in indoor air and wastewater: the role of residential washing machines. *J Air Waste Manage Assoc* 46(7):631-642.
- Smith, JH; Bomberger, DC, Jr; Haynes, DL. (1980) Prediction of the volatilization rates of high-volatility chemicals from natural water bodies. *Environ Sci Technol* 14(11):1332-1337.
- Tancrede, MV; Yanagisawa, Y; Wilson, R. (1992) Volatilization of volatile organic compounds from showers. I: analytical method and quantitative assessment. *Atmos Environ* 26A(6):1103-1111.
- Tucker, WA; Nelken, LH. (1990) Diffusion coefficients in air and water. In: *Handbook of chemical property estimation methods*. Lyman, WH; Reehl, WF; Rosenblatt, DH, eds. Washington, DC: American Chemical Society, pp. 17-1-17-25.
- Wooley, J; Nazaroff, WW; Hodgson, AT. (1990) Release of ethanol to the atmosphere during use of consumer cleaning products. *J Air Waste Manage Assoc* 40:1114-1120.

APPENDIX:
CHEMICAL VOLATILIZATION DATABASE

Equations to Solve Mass Transfer Parameters In Database

General Equations Applied to All Applicable Sources:

Chemical Stripping Efficiency = $\eta = \left(1 - \frac{C_i}{C_{i,0}}\right) \times 100\%$

Variables

C_i =	chemical concentration in liquid phase out of system	Units mg/L
$C_{i,0}$ =	chemical concentration in liquid phase entering system	mg/L

Mass Closure Estimate = % mass recovered = $\frac{V_1 C_{i,2} + V_2 C_{g,2} + Q_g \int_{t_1}^{t_2} C_g dt}{V_1 C_{i,1} + V_2 C_{g,1}}$

Variables

V_1 =	liquid volume	Units L
$C_{i,1}$ =	chemical concentration in liquid phase at time 1	mg/L
$C_{i,2}$ =	chemical concentration in liquid phase at time 2	mg/L
V_g =	headspace volume	L
$C_{g,1}$ =	chemical concentration in gas phase at time 1	mg/L
$C_{g,2}$ =	chemical concentration in gas phase at time 2	mg/L
Q_g =	ventilation rate of system	L/min
t_1 =	time 1	min
t_2 =	time 2	min

k_g/k_l Matrix Method

$K_L A_i$	Chemical 1	Chemical 2	Chemical 3	Chemical 4	Chemical n
Chemical 1	1				
Chemical 2		1			
Chemical 3			1		
Chemical 4				1	
Chemical n					1

Variables

$K_L A_i$ =	overall mass transfer value for chemical "i"	Units L/min
$K_L A_j$ =	overall mass transfer value for chemical "j"	L/min
Ψ_i =	$(D_l/D_g)^{n_i}$	
D_l =	liquid-phase diffusion coefficient for chemical "i"	cm ² /sec
D_g =	liquid-phase diffusion coefficient for chemical "j"	cm ² /sec
n_i =	liquid-phase power constant	
Ψ_g =	$(D_g/D_l)^{n_g}$	
D_{gl} =	gas-phase diffusion coefficient for chemical "i"	cm ² /sec
D_{gl} =	gas-phase diffusion coefficient for chemical "j"	cm ² /sec
n_g =	liquid-phase power constant	
H_{ci} =	Henry's law constant for chemical "i"	m ³ liquid/m ³ gas
H_{cj} =	Henry's law constant for chemical "j"	m ³ liquid/m ³ gas
k_{gl}/k_l =	ratio of liquid- and gas-phase mass transfer coefficients for chemical "j"	

Three $n \times n$ matrices were filled with the following values:

Matrix 1: Ratio of measured $K_L A_i/K_L A_j$ values for all chemicals and single experimental condition

Matrix 2: Ratio of predicted $K_L A_i/K_L A_j$ values for all chemicals using an assumed k_g/k_l value in the following equation:

$$\frac{K_L A_i}{K_L A_j} = \Psi_i \Psi_j \left\{ \frac{H_{ci}}{H_{cj}} \right\} \left\{ \frac{1 + \left[\frac{k_{gl}}{k_l} \right] H_{cj}}{\Psi_i + \Psi_j H_{ci} \left[\frac{k_{gl}}{k_l} \right]} \right\}$$

Matrix 3: Normalized residual between values in corresponding cells of Matrix 1 and Matrix 2.

Each column and row of this matrix was added to find the total residual to be minimized.

The value of k_g/k_l used to predict $K_L A$ values in Matrix 2 was used to minimize total residual. Minimum residual value corresponded to "best" k_g/k_l value.

Use k_g/k_l value and $\frac{1}{K_L A} = \frac{1}{k_L A} + \frac{1}{k_g A \cdot H_c}$ to solve for liquid-phase mass transfer coefficient ($k_L A$) and gas-phase mass transfer coefficient ($k_g A$)

Solution Methods for Values of K_{LA} Referenced in Database

Method #

1

Applicable Sources: Shower, Flow-through Bathtub

Model Equation:
$$C_{t,out} = C_{t,in} \exp \left(- \frac{K_{LA}}{Q_l} \right) + \left(\frac{C_g}{H_c} \right) \left(1 - \exp \left(- \frac{K_{LA}}{Q_l} \right) \right)$$

 Predicts $C_{t,out}$

Variables

$C_{t,out}$ = chemical concentration in liquid-phase exiting system
 $C_{t,in}$ = chemical concentration in liquid-phase entering system
 K_{LA} = overall mass transfer coefficient multiplied by interfacial area
 Q_l = system liquid flowrate
 C_g = chemical concentration in gas-phase of system at time t
 H_c = Henry's law coefficient of chemical

Units

mg/L
 mg/L
 L/min
 L/min
 mg/L
 (L³/L³-gas)

$$\left[\frac{(C_{t,out, measured} - C_{t,out, predicted})}{C_{t,out, measured}} \right]^2$$

Solution Technique: Solve for K_{LA} by minimizing normalized residual between measured $C_{t,out}$ and predicted $C_{t,out}$

2

Applicable Sources: Shower, Flow-through Bathtub

Model Equation:
$$C_s = \frac{a}{b} + \left(C_{s,in} - \frac{a}{b} \right) \exp(-bt)$$

 Predicts C_g

where:

$$a = \frac{\left(Q_l C_{t,in} \left(1 - \exp \left(- \frac{K_{LA}}{Q_l} \right) \right) + Q_g C_{g,u} \right)}{V_s}$$

$$b = \frac{\left(\frac{Q_l}{H_c} \right) \left[\left(1 - \exp \left(- \frac{K_{LA}}{Q_l} \right) \right) + Q_g \right]}{V_s}$$

Units

mg/L
 mg/L
 L/min
 mg/L
 L/min
 L/min
 L
 (L³/L³-gas)

Variables

C_g = chemical concentration in gas-phase
 $C_{g,u}$ = chemical concentration in gas-phase at start of experiment
 Q_l = system liquid flowrate
 $C_{t,in}$ = chemical concentration in liquid-phase entering system
 K_{LA} = overall mass transfer coefficient multiplied by interfacial area
 Q_g = system ventilation rate
 V_g = headspace volume
 H_c = Henry's law constant of chemical

$$\left[\frac{(C_{g, measured} - C_{g, predicted})}{C_{g, measured}} \right]^2$$

Solution Technique: Solve for K_{LA} by minimizing normalized residual between measured C_g and predicted C_g

Applicable Sources: Washing Machine Fill Cycle, Filling Bathroom

Model Equations:

Predicts C_l and C_g

Discretized Equations:

$$C_l^{n+1} = \left[\frac{Q_l C_{l,in}}{V_l^n} - \frac{Q_l C_l^n}{V_l^n} - \frac{K_L A C_l^n}{V_l^n} + \frac{K_L A C_g^n}{V_l^n H_c} \right] \Delta t + C_l^n$$

$$C_g^{n+1} = \left[\frac{-Q_g C_g^n}{(V_l - V_g^n)} + \frac{Q_g C_l^n}{(V_l - V_g^n)} + \frac{K_L A C_l^n}{(V_l - V_g^n)} - \frac{K_L A C_g^n}{(V_l - V_g^n) H_c} \right] \Delta t + C_g^n$$

2nd Order Runge-Kutta Technique:

$$C^{n+1} = C^n + \frac{\Delta t}{2} \left\{ f(t^n, C^n) + f\left[t^n + \Delta t, C^n + \Delta t f(t^n, C^n)\right] \right\}$$

Solution Technique:

Solve for $K_L A$ by minimizing normalized residual between measured C_l^{n+1} or C_g^{n+1} and predicted values at associated time steps.
Note: Liquid-phase concentration equation is dependent on gas-phase concentration

$$\left[\frac{C_{l, \text{measured}} - C_{l, \text{predicted}}}{C_{l, \text{measured}}} \right]^2$$

Variables	Units
C_l^n =	chemical concentration in liquid phase at time step n mg/L
C_l^{n+1} =	chemical concentration in liquid phase at time step n+1 mg/L
V_l^n =	liquid volume at time step n L
V_l =	total volume of system L
$K_L A$ =	overall mass transfer coefficient multiplied by interfacial area L/min
Q_l =	system liquid flowrate L/min
$C_{l,0}$ =	chemical concentration in liquid-phase entering system mg/L
H_c =	Henry's law constant of chemical (L _g /L _{gas})
C_g^n =	chemical concentration in gas phase at time step n mg/L
C_g^{n+1} =	chemical concentration in gas phase at time step n+1 mg/L
Q_g =	system ventilation rate L/min
Δt =	differential time step min

Applicable Sources: Dishwasher, Washing Machine Wash/Rinse Cycle, Handwashing Dishes in Kitchen Sink, Bathing

Model Equation:

Predicts C_l

where:

$$C_l = C_{l,0} \left[\exp \left(-\frac{D}{2} t \right) \cosh \left(\left(\sqrt{\frac{D^2}{4} - E} \right) t \right) \right] + \left(\frac{BF}{Z} + \frac{EC_{l,0}}{Z} - \frac{DC_{l,0}}{2} \right) \left[\frac{1}{\sqrt{\frac{D^2}{4} - E}} \exp \left(-\frac{D}{2} t \right) \sinh \left(\left(\sqrt{\frac{D^2}{4} - E} \right) t \right) \right]$$

$$Z = \frac{K_L A}{V_l}$$

$$B = \frac{K_L A}{V_l H_c}$$

$$X = \frac{K_L A}{V_g}$$

$$Y = \frac{Q_g}{V_g} + \frac{K_L A}{V_g H_c}$$

$$D = Z + Y$$

$$E = ZY - BX$$

$$F = ZC_{g,0} + XC_{l,0}$$

Variables

C_l = chemical concentration in liquid phase

$C_{l,0}$ = initial chemical concentration in liquid phase

$K_L A$ = overall mass transfer coefficient multiplied by interfacial area

V_l = system liquid volume

H_c = Henry's law constant of chemical

V_g = system headspace volume

Q_g = system ventilation rate

$C_{g,0}$ = initial chemical concentration in gas phase

t = time

Units
mg/L
mg/L
L/min
L
(L _g /L _{gas})
L
L/min
mg/L
min

Solution Technique:

Solve for $K_L A$ by minimizing residual between measured C_l and predicted C_l

$$\left[\frac{C_{l, \text{measured}} - C_{l, \text{predicted}}}{C_{l, \text{measured}}} \right]^2$$

Applicable Sources: Dishwasher, Washing Machine Wash/Rinse Cycle, Handwashing Dishes in Kitchen Sink, Bathing

Model Equation: $C_s = C_{s0} \exp\left(-\frac{D}{2}t\right) \cosh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right) + \left(F - \frac{DC_{s0}}{2}\right) \left[\frac{1}{\left(\sqrt{\frac{D^2}{4} - E}\right)} \exp\left(-\frac{D}{2}t\right) \sinh\left(\left(\sqrt{\frac{D^2}{4} - E}\right)t\right)\right]$
 Predicts C_g

where:	$Z = \frac{K_L A}{V_l}$	$B = \frac{K_L A}{V_l H_c}$	$X = \frac{K_L A}{V_g}$	Variables	Units
	$Y = \frac{Q_g + K_L A}{V_g}$	$D = Z + Y$	$E = ZY - BX$	C_g = chemical concentration in gas phase	mg/L
				C_{g0} = initial chemical concentration in gas phase	mg/L
				$K_L A$ = overall mass transfer coefficient multiplied by interfacial area	L/min
				V_l = system liquid volume	L
				H_c = Henry's law constant of chemical	(L ³ /L ³ -gas)
				V_g = system headspace volume	L
				Q_g = system ventilation rate	L/min
				C_{l0} = initial chemical concentration in liquid phase	mg/L
				t = time	min
	$F = ZC_{g0} + XC_{l0}$				

Solution Technique: Solve for $K_L A$ by minimizing residual between measured C_g and predicted C_g :
$$\left[\frac{(C_{g, \text{measured}} - C_{g, \text{predicted}})}{C_{g, \text{measured}}} \right]^2$$

Applicable Sources: Kitchen Sink (with recirculating batch reactor experimental design)

Model Equation: Predicts C_l	$C_l = C_{l0} \exp(-K_L a t)$	Variables	Units
		C_l = chemical concentration in liquid phase at time t	mg/L
		C_{l0} = initial chemical concentration in liquid phase	mg/L
		$K_L a$ = overall mass transfer coefficient multiplied by interfacial area/liquid volume	min ⁻¹
		t = time	min

Solution Technique: Slope of best curve fit of $\ln(C_l/C_{l0})$ vs. time equal to $K_L a$
 Chemical stripping efficiencies also solved using best fit equation to measured liquid data according to: $C_l = C_{l0} \exp\left(-\frac{t}{\theta_s} - \eta\right)$

SHOWER DATABASE

STUDY: Moya, J, Howard-Reed, C, and Corsi, R.L.
Study year: 1999
Reference: *Environmental Science and Technology*, Vol. 33, 1999, pp. 2321-2327
Solution Methods: Method 1 for acetone, ethyl acetate, toluene, ethylbenzene, cyclohexane
Assumptions: None
Comments: Values of η and K_A are averages of values determined for three separate time periods within experiment.
 Mass closure based on liquid standard curve created using well-dissolved tracer bag.

* = Could not be determined with available data; n/m = not measured.

Entry #
1

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters				
Spray Type =	coarse	Chemical	H_e @ 21 C D_L @ 24 C D_g @ 24 C (m^3 gas / m^3 gas) (cm ² /sec) (cm ² /sec)	C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,out}$ (mg/L)	η (%)	K_A (L/min)	K_A (L/min)	K_g/K_L (L/min)	Mass Closure (%)
Duration (min) =	8	Acetone	0.0010 1.1×10^{-5} 0.11	38	34-37	0	0.036	6.3	1.8	13	1086	153
Liquid Temperature (C) =	21	Ethyl Acetate	0.0042 9.5×10^{-6} 0.092	26	20-24	0	0.068	15	2.9	7.3	1111	153
Liquid Flowrate (L/min) =	8.1	Toluene	0.24 9.1×10^{-6} 0.085	4.5	1.8	0	0.041	61	8.8	9	1380	153
Gas Flowrate (L/min) =	370	Ethylbenzene	0.27 8.4×10^{-6} 0.077	6.1	2.3	0	0.029	62	8.9	9.1	1395	153
Shower Stall Volume (L) =	1745	Cyclohexane	6.5 9.0×10^{-6} 0.088	1.9	0.63	0	0.0068	65	9.6	9.6	1468	153
Person Present =	No											76

2

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters				
Spray Type =	fine	Chemical	H_e @ 22 C D_L @ 24 C D_g @ 24 C (m^3 gas / m^3 gas) (cm ² /sec) (cm ² /sec)	C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,out}$ (mg/L)	η (%)	K_A (L/min)	K_A (L/min)	K_g/K_L (L/min)	Mass Closure (%)
Duration (min) =	8	Acetone	0.0011 1.1×10^{-5} 0.11	42	35-40	0	0.041	8.4	3.0	16	3519	223
Liquid Temperature (C) =	22	Ethyl Acetate	0.0044 9.5×10^{-6} 0.092	22	16-20	0	0.081	15	4.0	8.1	1807	223
Liquid Flowrate (L/min) =	9.1	Toluene	0.25 9.1×10^{-6} 0.085	7.0	2.3	0	0.057	68	11	11	2434	223
Gas Flowrate (L/min) =	343	Ethylbenzene	0.27 8.4×10^{-6} 0.077	7.3	2.3	0	0.032	68	11	11	2384	223
Shower Stall Volume (L) =	1745	Cyclohexane	6.5 9.0×10^{-6} 0.088	3.9	0.88	0	0.0097	73	12	12	2652	223
Person Present =	No											68

3

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters				
Spray Type =	coarse	Chemical	H_e @ 21 C D_L @ 24 C D_g @ 24 C (m^3 gas / m^3 gas) (cm ² /sec) (cm ² /sec)	C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,out}$ (mg/L)	η (%)	K_A (L/min)	K_A (L/min)	K_g/K_L (L/min)	Mass Closure (%)
Duration (min) =	8	Acetone	0.0010 1.1×10^{-5} 0.11	42	35-39	0	0.035	9.1	1.4	8.8	1723	200
Liquid Temperature (C) =	21	Ethyl Acetate	0.0044 9.5×10^{-6} 0.092	26	19-22	0	0.057	20	2.3	5.1	1030	200
Liquid Flowrate (L/min) =	6.1	Toluene	0.24 9.1×10^{-6} 0.085	7.0	2.5	0	0.029	63	6.2	6.4	1274	200
Gas Flowrate (L/min) =	360	Ethylbenzene	0.26 8.4×10^{-6} 0.077	7.5	2.8	0	0.011	63	6.0	6.2	1234	200
Shower Stall Volume (L) =	1745	Cyclohexane	6.3 9.0×10^{-6} 0.088	3.0	1.0	0	0.0079	66	6.5	6.5	1305	200
Person Present =	No											77

4

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters				
Spray Type =	fine	Chemical	H_e @ 22 C D_L @ 24 C D_g @ 24 C (m^3 gas / m^3 gas) (cm ² /sec) (cm ² /sec)	C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,out}$ (mg/L)	η (%)	K_A (L/min)	K_A (L/min)	K_g/K_L (L/min)	Mass Closure (%)
Duration (min) =	8	Acetone	0.0011 1.1×10^{-5} 0.11	43	37-41	0	0.037	9.3	1.5	8.8	1720	195
Liquid Temperature (C) =	22	Ethyl Acetate	0.0044 9.5×10^{-6} 0.092	31	22-26	0	0.083	20	2.5	5.3	1031	195
Liquid Flowrate (L/min) =	6.1	Toluene	0.25 9.1×10^{-6} 0.085	6.1	2.2	0	0.038	64	6.4	6.5	1275	195
Gas Flowrate (L/min) =	360	Ethylbenzene	0.26 8.4×10^{-6} 0.077	5.5	2.0	0	0.018	63	6.2	6.3	1232	195
Shower Stall Volume (L) =	1745	Cyclohexane	6.7 9.0×10^{-6} 0.088	2.0	0.67	0	0.0083	66	6.7	6.7	1308	195
Person Present =	No											85

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =		H_e @ 35 C	D_l @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	η	k_dA	Mass Closure
Duration (min) =	coarse	(m^3/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(%)
Liquid Temperature (C) =	8	0.0022	1.1×10^{-5}	0.11	42	34 - 38	0	0.077	13	2.8	14
Liquid Flowrate (L/min) =	35	0.0077	9.5×10^{-6}	0.092	24	16 - 19	0	0.13	27	5.5	12
Gas Flowrate (L/min) =	9.1	0.37	9.1×10^{-6}	0.085	6.4	2.0	0	0.056	68	11	11
Shower Stall Volume (L) =	379	0.54	8.4×10^{-6}	0.077	8.0	2.5	0	0.032	68	11	11
Person Present =	1745	10	9.0×10^{-6}	0.088	2.6	0.63	0	0.0093	75	13	13
	No										

5

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =		H_e @ 34 C	D_l @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	η	k_dA	Mass Closure
Duration (min) =	fine	(m^3/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(%)
Liquid Temperature (C) =	8	0.0021	1.1×10^{-5}	0.11	40	34 - 38	0	0.071	11	3.4	16
Liquid Flowrate (L/min) =	34	0.0074	9.5×10^{-6}	0.092	24	15 - 18	0	0.12	28	6.9	14
Gas Flowrate (L/min) =	9.1	0.35	9.1×10^{-6}	0.085	5.3	1.3	0	0.053	75	13	14
Shower Stall Volume (L) =	354	0.51	8.4×10^{-6}	0.077	4.6	1.1	0	0.031	75	13	13
Person Present =	1745	9.6	9.0×10^{-6}	0.088	1.6	0.35	0	0.0054	77	14	14
	No										

6

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =		H_e @ 34 C	D_l @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	η	k_dA	Mass Closure
Duration (min) =	fine	(m^3/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(%)
Liquid Temperature (C) =	8	0.0021	1.1×10^{-5}	0.11	40	32 - 37	0	0.071	12	3.7	15
Liquid Flowrate (L/min) =	34	0.0074	9.5×10^{-6}	0.092	25	15 - 19	0	0.13	29	6.7	13
Gas Flowrate (L/min) =	9.1	0.36	9.1×10^{-6}	0.085	5.2	1.3	0	0.058	74	12	13
Shower Stall Volume (L) =	373	0.52	8.4×10^{-6}	0.077	3.8	1.0	0	0.031	74	12	12
Person Present =	1745	9.8	9.0×10^{-6}	0.088	0.71	0.17	0	0.0065	77	13	13
	No										

7

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =		H_e @ 36 C	D_l @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	η	k_dA	Mass Closure
Duration (min) =	coarse	(m^3/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(%)
Liquid Temperature (C) =	8	0.0024	1.1×10^{-5}	0.11	41	32 - 36	0	0.054	16	2.2	11
Liquid Flowrate (L/min) =	36	0.0080	9.5×10^{-6}	0.092	24	14 - 17	0	0.081	32	3.8	8.2
Gas Flowrate (L/min) =	6.1	0.38	9.1×10^{-6}	0.085	5.6	1.5	0	0.036	74	8.4	8.6
Shower Stall Volume (L) =	364	0.57	8.4×10^{-6}	0.077	5.3	1.4	0	0.023	73	8.2	8.3
Person Present =	1745	10	9.0×10^{-6}	0.088	1.9	0.46	0	0.0054	76	8.6	8.6
	No										

8

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =		H_e @ 35 C	D_l @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	η	k_dA	Mass Closure
Duration (min) =	fine	(m^3/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(%)
Liquid Temperature (C) =	8	0.0022	1.1×10^{-5}	0.11	42	33 - 37	0	0.079	14	2.3	9.6
Liquid Flowrate (L/min) =	35	0.0077	9.5×10^{-6}	0.092	24	14 - 18	0	0.12	33	4.7	9.0
Gas Flowrate (L/min) =	6.1	0.36	9.1×10^{-6}	0.085	6.0	1.6	0	0.048	73	8.1	8.3
Shower Stall Volume (L) =	371	0.53	8.4×10^{-6}	0.077	5.6	1.5	0	0.029	72	7.9	8.0
Person Present =	1745	10	9.0×10^{-6}	0.088	1.8	0.43	0	0.0060	75	8.4	8.4
	No										

9

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = fine	$H_c @ 34\text{ C}$ $D_1 @ 24\text{ C}$ $D_2 @ 24\text{ C}$ $D_3 @ 24\text{ C}$	C_{in} C_{out} $C_{g, in}$ $C_{g, end}$	η $K_L A$ $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 8	Chemical (m^3/m^3) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 34	Acetone 0.0021 1.1×10^{-5} 0.11	40 32-37 0 0.081	15 2.5 11 1507 138 103
Liquid Flowrate (L/min) = 6.1	Ethyl Acetate 0.0074 9.5×10^{-6} 0.092	24 14-16 0 0.13	36 5.3 10 1443 138 105
Gas Flowrate (L/min) = 387	Toluene 0.36 9.1×10^{-5} 0.085	5.4 1.3 0 0.047	77 9.2 9.3 1291 138 88
Shower Stall Volume (L) = 1745	Ethylbenzene 0.53 8.4×10^{-5} 0.077	4.5 1.1 0 0.027	75 8.8 8.9 1227 138 75
Person Present = No	Cyclohexane 9.9 9.0×10^{-5} 0.088	0.84 0.17 0 0.0957	90 9.9 9.9 1365 138 80

STUDY:

Study year: 1997

Reference: *Atmospheric Environment*, Vol. 31, No. 2, 1997, pp. 123-130

Solution Methods: Method 1

Assumptions: $C_{g, in} = 0$

Comments: $C_{g, end}$ values picked off graph presented in paper.

C_{out} and C_{in} were measured in triplicate at 2, 4, and 8 minutes at the drain and shower nozzle, respectively.

Resulting measurements at each sample location, respectively, were not found to be statistically different, so values listed are averages for three sample times. Results for studies 11, 12, 14, and 16 are based on three different experiments.

Results for studies 13 and 15 are based on two different experiments. (Individual results not given in paper — only averages).

Liquid flowrate value of 3.5 L/min is average of range of values given in paper (3.1 L/min to 3.8 L/min).

* = Could not be determined with available data; n/m = not measured

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = "spray"	$H_c @ 40\text{ C}$ $D_1 @ 24\text{ C}$ $D_2 @ 24\text{ C}$ $D_3 @ 24\text{ C}$	C_{in} C_{out} $C_{g, in}$ $C_{g, end}$	η $K_L A$ $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 10	Chemical (m^3/m^3) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 40	Chloroform 0.37 9.7×10^{-5} 0.10	64 11 0 0.31	83 6.7 * * * 52
Liquid Flowrate (L/min) = 3.5	Chloroform 0.37 9.7×10^{-5} 0.10	57 20 0 0.31	65 3.8 * * * 74
Gas Flowrate (L/min) = 185			
Shower Stall Volume (L) = 1530			
Person Present = No			

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = "jet"	$H_c @ 40\text{ C}$ $D_1 @ 24\text{ C}$ $D_2 @ 24\text{ C}$ $D_3 @ 24\text{ C}$	C_{in} C_{out} $C_{g, in}$ $C_{g, end}$	η $K_L A$ $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 10	Chemical (m^3/m^3) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 40	Chloroform 0.37 9.7×10^{-5} 0.10	56 16 0 0.44	66 4.2 * * * 88
Liquid Flowrate (L/min) = 3.5			
Gas Flowrate (L/min) = 185			
Shower Stall Volume (L) = 1530			
Person Present = No			

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = 1800 μL	$H_c @ 35\text{ C}$ $D_1 @ 24\text{ C}$ $D_2 @ 24\text{ C}$ $D_3 @ 24\text{ C}$	C_{in} C_{out} $C_{g, in}$ $C_{g, end}$	η $K_L A$ $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 10	Chemical (m^3/m^3) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 35	Chloroform 0.29 9.7×10^{-5} 0.10	57 9.4 0 0.58	89 9.1 * * * 84
Liquid Flowrate (L/min) = 3.5			
Gas Flowrate (L/min) = 185			
Shower Stall Volume (L) = 1530			
Person Present = No			

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = 1800 µl	$H_e @ 45^\circ C$ $D_1 @ 24^\circ C$ $D_2 @ 24^\circ C$	C_{in} C_{out} $C_{g,in}$ $C_{g,out}$	η K_dA k_dA k_g/k_l Mass Closure (%)
Duration (min) = 10	Chemical (m^3/m^3_{gas}) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 45	Chloroform 0.47×10^{-3} 0.10	56 5.1 0 0.48	81 8.7 . . . 87
Liquid Flowrate (L/min) = 3.5			
Gas Flowrate (L/min) = 195			
Shower Stall Volume (L) = 1530			
Person Present = No			

14

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = 300 µl	$H_e @ 35^\circ C$ $D_1 @ 24^\circ C$ $D_2 @ 24^\circ C$	C_{in} C_{out} $C_{g,in}$ $C_{g,out}$	η K_dA k_dA k_g/k_l Mass Closure (%)
Duration (min) = 10	Chemical (m^3/m^3_{gas}) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 35	Chloroform 0.29×10^{-3} 0.10	60 14 0 0.53	77 6.5 . . . 87
Liquid Flowrate (L/min) = 3.5			
Gas Flowrate (L/min) = 195			
Shower Stall Volume (L) = 1530			
Person Present = No			

15

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = 300 µl	$H_e @ 45^\circ C$ $D_1 @ 24^\circ C$ $D_2 @ 24^\circ C$	C_{in} C_{out} $C_{g,in}$ $C_{g,out}$	η K_dA k_dA k_g/k_l Mass Closure (%)
Duration (min) = 10	Chemical (m^3/m^3_{gas}) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 45	Chloroform 0.47×10^{-3} 0.10	51 10 0 0.54	80 8.0 . . . 95
Liquid Flowrate (L/min) = 3.5			
Gas Flowrate (L/min) = 195			
Shower Stall Volume (L) = 1530			
Person Present = No			

16

STUDY:

Giardino and Andelman

1996

Reference: *Journal of Exposure Analysis and Environmental Epidemiology*, Vol. 6, No. 4, 1996, pp. 413-423.

Solution Method: Method 1

Assumptions:

 $C_{g,in} = 0$.No C_{out} values were reported; assumed it was equal to $(1-\eta) \times C_{in}$, where η is given in paper. C_{out} remained relatively constant for entire experiment. C_{in} is reported average value for 10-minute experiment. Thus, η is an average value for 10-minute period.

Comments:

* = Could not be determined with available data; n/m = not measured.

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_e @ 27^\circ C$ $D_1 @ 24^\circ C$ $D_2 @ 24^\circ C$	C_{in} C_{out} $C_{g,in}$ $C_{g,out}$	η K_dA k_dA k_g/k_l Mass Closure (%)
Duration (min) = 23	Chemical (m^3/m^3_{gas}) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	
Liquid Temperature (C) = 27	Trichloroethylene 0.46×10^{-3} 0.084	0.49 0.160 0 0.020	67 6.3 . . . 121
Liquid Flowrate (L/min) = 5.0			
Gas Flowrate (L/min) = 88			
Shower Volume (L) = 1520			
Person Present = No			

17

18

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	H _c @ 22 C D ₁ @ 24 C D _g @ 24 C	C _{in} C _{out} C _{g,in} C _{g,end}	η K _A k _A k _{gA} k _{g/k_i} Mass Closure (%)
Duration (min) = 22	Chemical (m ³ _{liq} /m ³ _{gas}) (cm ² /sec) (cm ² /sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 22	Trichloroethene 0.35 9.4 x 10 ⁻⁶ 0.084	0.96 0.380 0 0.014	60 5.0 * * * 99
Liquid Flowrate (L/min) = 5.1			
Gas Flowrate (L/min) = 270			
Shower Volume (L) = 1500			
Person Present = No			

19

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	H _c @ 21 C D ₁ @ 24 C D _g @ 24 C	C _{in} C _{out} C _{g,in} C _{g,end}	η K _A k _A k _{gA} k _{g/k_i} Mass Closure (%)
Duration (min) = 10	Chemical (m ³ _{liq} /m ³ _{gas}) (cm ² /sec) (cm ² /sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 21	Trichloroethene 0.33 9.4 x 10 ⁻⁶ 0.084	0.49 0.210 0 0.043	57 12 * * * 125
Liquid Flowrate (L/min) = 9.9			
Gas Flowrate (L/min) = 28			
Shower Volume (L) = 1500			
Person Present = No			

20

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	H _c @ 19 C D ₁ @ 24 C D _g @ 24 C	C _{in} C _{out} C _{g,in} C _{g,end}	η K _A k _A k _{gA} k _{g/k_i} Mass Closure (%)
Duration (min) = 19	Chemical (m ³ _{liq} /m ³ _{gas}) (cm ² /sec) (cm ² /sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 19	Trichloroethene 0.30 9.4 x 10 ⁻⁶ 0.084	0.42 0.180 0 0.0015	57 9.6 * * * 112
Liquid Flowrate (L/min) = 10			
Gas Flowrate (L/min) = 240			
Shower Volume (L) = 1500			
Person Present = No			

21

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	H _c @ 46 C D ₁ @ 24 C D _g @ 24 C	C _{in} C _{out} C _{g,in} C _{g,end}	η K _A k _A k _{gA} k _{g/k_i} Mass Closure (%)
Duration (min) = 19	Chemical (m ³ _{liq} /m ³ _{gas}) (cm ² /sec) (cm ² /sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 46	Trichloroethene 1.1 9.4 x 10 ⁻⁶ 0.084	0.92 0.180 0 0.042	81 8.9 * * * 129
Liquid Flowrate (L/min) = 5.0			
Gas Flowrate (L/min) = 83			
Shower Volume (L) = 1500			
Person Present = No			

22

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	H _c @ 44 C D ₁ @ 24 C D _g @ 24 C	C _{in} C _{out} C _{g,in} C _{g,end}	η K _A k _A k _{gA} k _{g/k_i} Mass Closure (%)
Duration (min) = 19	Chemical (m ³ _{liq} /m ³ _{gas}) (cm ² /sec) (cm ² /sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 44	Trichloroethene 1.0 9.4 x 10 ⁻⁶ 0.084	0.59 0.110 0 0.014	81 8.5 * * * 119
Liquid Flowrate (L/min) = 5.0			
Gas Flowrate (L/min) = 270			
Shower Volume (L) = 1500			
Person Present = No			

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_e @ 33\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	η (%)
Duration (min) = 19	0.62	C_{out} (mg/L)	k_A (L/min)
Liquid Temperature (C) = 33	9.4×10^{-8}	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 10		0	74
Gas Flowrate (L/min) = 28		0.130	20
Shower Volume (L) = 1500			124
Person Present = No			

23

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_e @ 32\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	η (%)
Duration (min) = 19	0.59	C_{out} (mg/L)	k_A (L/min)
Liquid Temperature (C) = 32	9.4×10^{-8}	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 9.9		0	66
Gas Flowrate (L/min) = 225		0.30	12
Shower Volume (L) = 1500			107
Person Present = No			

24

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_e @ 25\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	η (%)
Duration (min) = 19	0.41	C_{out} (mg/L)	k_A (L/min)
Liquid Temperature (C) = 25	9.4×10^{-8}	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 9.9		0	59
Gas Flowrate (L/min) = 33		0.330	12
Shower Volume (L) = 1500			112
Person Present = No			

25

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_e @ 26\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	η (%)
Duration (min) = 11	0.18	C_{out} (mg/L)	k_A (L/min)
Liquid Temperature (C) = 26	9.7×10^{-8}	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 5.0		0	44
Gas Flowrate (L/min) = 70		0.360	3.2
Shower Volume (L) = 1500			116
Person Present = No			

26

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_e @ 42\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	η (%)
Duration (min) = 11	0.35	C_{out} (mg/L)	k_A (L/min)
Liquid Temperature (C) = 42	9.7×10^{-8}	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 5.0		0	62
Gas Flowrate (L/min) = 65		0.220	5.3
Shower Volume (L) = 1500			131
Person Present = No			

27

28

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 27\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_p A$ k_g/k_L Mass Closure (%)
Duration (min) = 11	$(m^3/m^3_{gas}) (cm^2/sec)$	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 27	0.19 9.7×10^{-5} 0.10	0.56 0.27 0 0.0077	52 4.0 * * 117
Liquid Flowrate (L/min) = 5.0			
Gas Flowrate (L/min) = 228			
Shower Volume (L) = 1500			
Person Present = No			

29

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 28\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_p A$ k_g/k_L Mass Closure (%)
Duration (min) = 11	$(m^3/m^3_{gas}) (cm^2/sec)$	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 28	0.20 9.7×10^{-5} 0.10	0.68 0.370 0 0.0025	46 7.9 * * 109
Liquid Flowrate (L/min) = 10			
Gas Flowrate (L/min) = 25			
Shower Volume (L) = 1500			
Person Present = No			

30

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 29\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_p A$ k_g/k_L Mass Closure (%)
Duration (min) = 11	$(m^3/m^3_{gas}) (cm^2/sec)$	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 29	0.20 9.7×10^{-5} 0.10	1.1 0.570 0 0.0020	49 3.7 * * 113
Liquid Flowrate (L/min) = 5.0			
Gas Flowrate (L/min) = 75			
Shower Volume (L) = 1500			
Person Present = No			

31

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 27\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_p A$ k_g/k_L Mass Closure (%)
Duration (min) = 10	$(m^3/m^3_{gas}) (cm^2/sec)$	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 27	0.01 7.6×10^{-5} 0.056	1.7 1.5 0 n/m	10 0.84 * * *
Liquid Flowrate (L/min) = 5.0			
Gas Flowrate (L/min) = 55			
Shower Volume (L) = 1500			
Person Present = No			

32

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 51\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_p A$ k_g/k_L Mass Closure (%)
Duration (min) = 14	$(m^3/m^3_{gas}) (cm^2/sec)$	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 51	0.05 7.6×10^{-5} 0.056	1.6 1.1 0 n/m	31 2.7 * * *
Liquid Flowrate (L/min) = 5.0			
Gas Flowrate (L/min) = 58			
Shower Volume (L) = 1500			
Person Present = No			

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 30\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	K_dA (L/min)
Duration (min) = 14	0.01	C_{out} (mg/L)	k_dA (L/min)
Liquid Temperature (C) = 30	7.6×10^{-6}	$C_{g,in}$ (mg/L)	k_d/k_l (L/min)
Liquid Flowrate (L/min) = 5.0		0	η (%)
Gas Flowrate (L/min) = 308		1.3	17
Shower Volume (L) = 1500		1.6	1.2
Person Present = No		n/m	*

33

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 42\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	K_dA (L/min)
Duration (min) = 12	0.03	C_{out} (mg/L)	k_dA (L/min)
Liquid Temperature (C) = 42	7.6×10^{-6}	$C_{g,in}$ (mg/L)	k_d/k_l (L/min)
Liquid Flowrate (L/min) = 5.0		0	η (%)
Gas Flowrate (L/min) = 53		1.3	20
Shower Volume (L) = 1500		1.7	1.6
Person Present = No		n/m	*

34

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 29\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	K_dA (L/min)
Duration (min) = 11	0.012	C_{out} (mg/L)	k_dA (L/min)
Liquid Temperature (C) = 29	7.6×10^{-6}	$C_{g,in}$ (mg/L)	k_d/k_l (L/min)
Liquid Flowrate (L/min) = 10		0	η (%)
Gas Flowrate (L/min) = 28		1.4	5.5
Shower Volume (L) = 1500		1.5	5.5
Person Present = No		n/m	*

35

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 32\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$ (m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)	C_{in} (mg/L)	K_dA (L/min)
Duration (min) = 11	0.015	C_{out} (mg/L)	k_dA (L/min)
Liquid Temperature (C) = 32	7.6×10^{-6}	$C_{g,in}$ (mg/L)	k_d/k_l (L/min)
Liquid Flowrate (L/min) = 5.0		0	η (%)
Gas Flowrate (L/min) = 88		2.4	13
Shower Volume (L) = 1500		2.8	0.97
Person Present = No		n/m	*

36

STUDY:

Giardino and Hageman

Study year:

1996

Reference:*Environmental Science and Technology*, Vol. 30, No. 4, 1996, pp.1242-1244**Solution Method:**

Method 1

Assumptions:No C_{out} values were reported; assumed it was equal to $(1-\eta) \times C_{in}$ where η is given in paper.The reported value of η is an average value based on pairs of influent and effluent liquid samples taken during experiment.**Comments:**

Liquid-phase diffusion coefficient estimated using relationship

$$\frac{D_{lin}}{D_{effluent}} = \left(\frac{MV_{effluent}}{MV_{lin}} \right)^{1/3}$$

* = Could not be determined with available data; n/m = not measured.

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =	unknown	H_c @ 22 C	D_i @ 24 C	D_g @ 24 C	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	k_g/k_L Mass Closure (%)
Duration (min) =	10	Chemical	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	1.1×10^{-4}	3.6×10^{-3}	0	48	67	4.5	51
Liquid Temperature (C) =	22	Radon	4.4	5.2×10^{-5}							
Liquid Flowrate (L/min) =	4.0										
Gas Flowrate (L/min) =	32										
Shower Volume (L) =	1510										
Person Present =	No										

37

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =	unknown	H_c @ 22 C	D_i @ 24 C	D_g @ 24 C	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	k_g/k_L Mass Closure (%)
Duration (min) =	10	Chemical	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	3.7×10^{-4}	1.1×10^{-3}	0	17	70	4.9	49
Liquid Temperature (C) =	22	Radon	4.4	5.2×10^{-5}							
Liquid Flowrate (L/min) =	4.0										
Gas Flowrate (L/min) =	36										
Shower Volume (L) =	1510										
Person Present =	No										

38

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =	unknown	H_c @ 22 C	D_i @ 24 C	D_g @ 24 C	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	k_g/k_L Mass Closure (%)
Duration (min) =	10	Chemical	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	2.1×10^{-4}	8.3×10^{-2}	0	3.6	61	1.9	53
Liquid Temperature (C) =	22	Radon	4.4	5.2×10^{-5}							
Liquid Flowrate (L/min) =	2.0										
Gas Flowrate (L/min) =	37										
Shower Volume (L) =	1510										
Person Present =	No										

39

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Spray Type =	unknown	H_c @ 22 C	D_i @ 24 C	D_g @ 24 C	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	k_g/k_L Mass Closure (%)
Duration (min) =	10	Chemical	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	3.1×10^{-4}	1.1×10^{-3}	0	9.5	64	2.0	62
Liquid Temperature (C) =	22	Radon	4.4	5.2×10^{-5}							
Liquid Flowrate (L/min) =	2.0										
Gas Flowrate (L/min) =	39										
Shower Volume (L) =	1510										
Person Present =	No										

40

STUDY:

Bernhardt and Hess

1995

Reference: Bernhardt's Master's Thesis for The University of Maine

Solution Method: Method 1

Assumptions: Shower stall and bathroom volumes were not given, so assumed a typical bathroom volume of 10000 L.
Shower curtain open for all experiments; thus used bathroom volume for V_g .

$$Q_g = 0$$

$$C_{g,p} = 0$$

Exact water temperature not given, so assumed $T = 23^\circ\text{C}$ for "cold" water.

Liquid-phase diffusion coefficient estimated using relationship given for Giordano and Hageman (1996).

* = Could not be determined with available data; n/m = not measured.

Comments:

41

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters		
Spray Type =	unknown	$H_c @ 23^\circ\text{C}$	$D_l @ 24^\circ\text{C}$	$D_g @ 24^\circ\text{C}$	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	η	k_A	Mass Closure
Duration (min) =	18	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	k_p/k_l
Liquid Temperature (C) =	23	4.4	5.2×10^{-6}	*	5.3×10^{-4}	1.5×10^{-4}	0	71	2.5	78
Liquid Flowrate (L/min) =	2.0									
Gas Flowrate (L/min) =	0									
Bathroom Volume (L) =	10000									
Person Present =	No									

42

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters		
Spray Type =	unknown	$H_c @ 23^\circ\text{C}$	$D_l @ 24^\circ\text{C}$	$D_g @ 24^\circ\text{C}$	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	η	k_A	Mass Closure
Duration (min) =	10	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	k_p/k_l
Liquid Temperature (C) =	23	4.4	5.2×10^{-6}	*	4.9×10^{-4}	5.7×10^{-3}	0	88	6.4	87
Liquid Flowrate (L/min) =	3.0									
Gas Flowrate (L/min) =	0									
Bathroom Volume (L) =	10000									
Person Present =	No									

43

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters		
Spray Type =	unknown	$H_c @ 23^\circ\text{C}$	$D_l @ 24^\circ\text{C}$	$D_g @ 24^\circ\text{C}$	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	η	k_A	Mass Closure
Duration (min) =	10	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	k_p/k_l
Liquid Temperature (C) =	23	4.35	5.2×10^{-6}	*	4.1×10^{-4}	9.0×10^{-3}	0	76	8.3	156
Liquid Flowrate (L/min) =	5.5									
Gas Flowrate (L/min) =	0									
Bathroom Volume (L) =	10000									
Person Present =	No									

44

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters		
Spray Type =	unknown	$H_c @ 23^\circ\text{C}$	$D_l @ 24^\circ\text{C}$	$D_g @ 24^\circ\text{C}$	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	η	k_A	Mass Closure
Duration (min) =	13	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	k_p/k_l
Liquid Temperature (C) =	23	4.35	5.2×10^{-6}	*	860	280	0	67	4.2	122
Liquid Flowrate (L/min) =	3.8									
Gas Flowrate (L/min) =	0									
Bathroom Volume (L) =	10000									
Person Present =	No									

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 23\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$ (m^3/m^3) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ (mg/L)	η (%)
Duration (min) = 12	Chemical	$C_{i,out}$ (mg/L)	k_A (L/min)
Liquid Temperature (C) = 23	Radon	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 3.2		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 0			
Bathroom Volume (L) = 10000			
Person Present = No			

45

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 23\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$ (m^3/m^3) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ (mg/L)	η (%)
Duration (min) = 9	Chemical	$C_{i,out}$ (mg/L)	k_A (L/min)
Liquid Temperature (C) = 23	Radon	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 3.2		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 0			
Bathroom Volume (L) = 10000			
Person Present = No			

46

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 23\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$ (m^3/m^3) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ (mg/L)	η (%)
Duration (min) = 11	Chemical	$C_{i,out}$ (mg/L)	k_A (L/min)
Liquid Temperature (C) = 23	Radon	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 3.2		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 0			
Bathroom Volume (L) = 10000			
Person Present = No			

47

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 23\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$ (m^3/m^3) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ (mg/L)	η (%)
Duration (min) = 13	Chemical	$C_{i,out}$ (mg/L)	k_A (L/min)
Liquid Temperature (C) = 23	Radon	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 6.0		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 0			
Bathroom Volume (L) = 10000			
Person Present = No			

48

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 23\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$ (m^3/m^3) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ (mg/L)	η (%)
Duration (min) = 10	Chemical	$C_{i,out}$ (mg/L)	k_A (L/min)
Liquid Temperature (C) = 23	Radon	$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 6.0		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 0			
Bathroom Volume (L) = 10000			
Person Present = No			

49

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 23\text{ C } D_i @ 24\text{ C } D_o @ 24\text{ C}$ ($\text{m}^3/\text{m}^3 \text{ gas}$) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,out}$	η $K_L A$ k_A $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 11	Chemical	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 23	Radon	1.4×10^{-3} 300 0 8.4	78 8.5 . . . 122
Liquid Flowrate (L/min) = 5.7			
Gas Flowrate (L/min) = 0			
Bathroom Volume (L) = 10000			
Person Present = No			

50

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 23\text{ C } D_i @ 24\text{ C } D_o @ 24\text{ C}$ ($\text{m}^3/\text{m}^3 \text{ gas}$) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,out}$	η $K_L A$ k_A $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 10	Chemical	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 23	Radon	1.3×10^{-3} 390 0 13	71 4.9 . . . 279
Liquid Flowrate (L/min) = 4.9			
Gas Flowrate (L/min) = 0			
Bathroom Volume (L) = 10000			
Person Present = No			

51

STUDY:

Hopke, Raunemaa, Daty, Kuusipalo, and Jensen
1995

Study year:
Reference: In Morawiska et al. *Indoor Air: An Integrated Approach*, Elsevier Science Ltd., 1995, pp. 107-110

Solution Method:
N/A

Assumptions:
 $C_{g,in} = 0$

Comments:
Liquid-phase diffusion coefficient estimated using relationship given for Giardini and Hageman (1996).
CPM = counts per minute measured with a liquid scintillation counter.
Not enough information given to calculate $K_L A$ or mass closure.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 32\text{ C } D_i @ 24\text{ C } D_o @ 24\text{ C}$ ($\text{m}^3/\text{m}^3 \text{ gas}$) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,out}$	η $K_L A$ k_A $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 15	Chemical	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 32	Radon	260 80 0 n/m	69
Liquid Flowrate (L/min) = not given			
Gas Flowrate (L/min) = 5			
Shower Volume (L) = 1765			
Person Present = No			

52

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 21\text{ C } D_i @ 24\text{ C } D_o @ 24\text{ C}$ ($\text{m}^3/\text{m}^3 \text{ gas}$) (cm^2/sec) (cm^2/sec)	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,out}$	η $K_L A$ k_A $k_g A$ k_g/k_L Mass Closure (%)
Duration (min) = 15	Chemical	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 21	Radon	130 37 0 n/m	71
Liquid Flowrate (L/min) = not given			
Gas Flowrate (L/min) = 20			
Shower Volume (L) = 1765			
Person Present = No			

53

STUDY: Keating and McKone

Study year: 1993

Reference: Modeling of Indoor Air Quality and Exposure, ASTM STP 1205, 1993, pp. 14-24

Solution Method: Method 1

Assumptions: $C_{g,0} = 0$

Comments: $C_{g,end}$ values visually picked off graph in paper.

Values for each nozzle represent average of three simulations.

* = Could not be determined with available data; n/m = not measured.

54

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = 1500 μ m	$H_c @ 45\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_f A$ $k_g A$ k_d/k_i Mass Closure (%)
Duration (min) = 8	Chemical (m^3/m^3) (cm^2/sec) (cm^2/sec) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(L/min) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 45	Trichloroethene 0.86 9.4×10^{-6} 0.084	0.21 0.030 0 0.0050	86 8.8 * * * 109
Liquid Flowrate (L/min) = 4.2			
Gas Flowrate (L/min) = 65			
Shower Stall Volume (L) = 1050			
Person Present = No			

55

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = 300 μ m	$H_c @ 45\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_f A$ $k_g A$ k_d/k_i Mass Closure (%)
Duration (min) = 10	Chemical (m^3/m^3) (cm^2/sec) (cm^2/sec) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(L/min) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 45	Trichloroethene 0.86 9.4×10^{-6} 0.084	0.22 0.0063 0 0.0037	97 14 * * * 86
Liquid Flowrate (L/min) = 2.8			
Gas Flowrate (L/min) = 65			
Shower Stall Volume (L) = 1050			
Person Present = No			

56

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = 1000 μ m	$H_c @ 45\text{ C } D_1 @ 24\text{ C } D_g @ 24\text{ C}$	$C_{i,in}$ $C_{i,out}$ $C_{g,in}$ $C_{g,end}$	η $K_L A$ $k_f A$ $k_g A$ k_d/k_i Mass Closure (%)
Duration (min) = 5	Chemical (m^3/m^3) (cm^2/sec) (cm^2/sec) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(L/min) (L/min) (L/min) (L/min) (%)
Liquid Temperature (C) = 45	Trichloroethene 0.86 9.4×10^{-6} 0.084	0.21 0.22 0 0.0032	72 15 * * * 72
Liquid Flowrate (L/min) = 6.0			
Gas Flowrate (L/min) = 65			
Shower Stall Volume (L) = 1050			
Person Present = No			

STUDY:

Study year:

Reference:

Solution Method:

Assumptions:

Comments:

Giardino, Esmen, and Ardelman

1992

Environmental Science and Technology, Vol. 26, 1992, pp.1602-1606

NIA

No $C_{1,at}$ values were reported, assumed it was equal to $(1-\eta) \times C_{1,at}$ where η is given in paper.

Shower had a vertical spray with no water impacting stall walls.

Not enough information given in the paper to calculate K_A values or mass closure.

Gas-phase concentration reported is average value for entire experiment.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = standard	$H_c @ 22\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{1,in}$ $C_{1,out}$ $C_{g,in}$ $C_{g,out}$	η K_A k_A k_g/k_l Mass Clos (%)
Duration (min) = not given	Chemical (m^3/m^3_{gas}) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 22	Trichloroethene 0.37 9.4×10^{-5} 0.084	0.46 0.15 0 0.025	67 * * * *
Liquid Flowrate (L/min) = 5			
Gas Flowrate (L/min) = 70			
Shower Stall Volume (L) = not given			
Person Present = No			

57

58

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = standard	$H_c @ 21\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{1,in}$ $C_{1,out}$ $C_{g,in}$ $C_{g,out}$	η K_A k_A k_g/k_l Mass Clos (%)
Duration (min) = not given	Chemical (m^3/m^3_{gas}) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 21	Trichloroethene 0.36 9.4×10^{-5} 0.084	0.78 0.32 0 0.080	59 * * * *
Liquid Flowrate (L/min) = 10			
Gas Flowrate (L/min) = 26			
Shower Stall Volume (L) = not given			
Person Present = No			

STUDY:

Study year:

Reference:

Solution Method:

Assumptions:

Comments:

Tancrede, Yanagisawa, and Wilson

1992

Atmospheric Environment, Vol. 26A, No. 6, 1992, pp. 1103-1111

Method 1

$C_{g,in} = 0$

$C_{1,in}$ is average of showerhead liquid samples collected at 2, 6, and 11 minutes.

$C_{1,out}$ is average of drain liquid samples collected at 8 and 12 minutes.

One C_g sample was collected at 10 minutes at nose level in the shower stall.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 25\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C}$	$C_{1,in}$ $C_{1,out}$ $C_{g,in}$ $C_{g,out}$	η K_A k_A k_g/k_l Mass Clos (%)
Duration (min) = 10	Chemical (m^3/m^3_{gas}) (cm^2/sec)	(mg/L) (mg/L) (mg/L) (mg/L)	(%) (L/min) (L/min) (L/min)
Liquid Temperature (C) = 25	CCl ₄ 1.2 9.2×10^{-5} 0.072	8.2×10^{-5} 5.0×10^{-5} 0 1.4×10^{-5}	39 7.0 7.2 205 29 82
Liquid Flowrate (L/min) = 13.6	PCE 0.74 8.5×10^{-5} 0.077	1.1×10^{-4} 4.9×10^{-5} 0 2.7×10^{-5}	56 12 13 365 29 345
Gas Flowrate (L/min) = 34.8	Trichloroethene 0.42 9.4×10^{-5} 0.084	0.0016 8.8×10^{-4} 0 4.9×10^{-5}	58 14 16 446 29 80
Shower Stall Volume (L) = 1491	Chloroform 0.17 9.7×10^{-5} 0.10	0.0026 0.0015 0 7.8×10^{-5}	42 11 13 372 29 94
Person Present = No	TCPA 0.012 7.9×10^{-5} 0.073	0.092 0.073 0 3.9×10^{-4}	21 2.5 9.8 281 29 85

59

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters				
Spray Type	$H_c @ 33^\circ\text{C}$ ($\text{m}^3/\text{m}^3_{\text{gas}}$)	$D_1 @ 24^\circ\text{C}$ (cm^2/sec)	$D_2 @ 24^\circ\text{C}$ (cm^2/sec)	$C_{1,\text{in}}$ (mg/L)	$C_{1,\text{out}}$ (mg/L)	$C_{9,\text{in}}$ (mg/L)	$C_{9,\text{end}}$ (mg/L)	η (%)	$k_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L	Mass Closure (%)		
unknown	10	1.7	9.2×10^{-6}	0.072	1.0×10^{-3}	2.5×10^{-3}	0	4.6×10^{-3}	76	21	22	412	19	78
	33													
	13.5	1.1	8.5×10^{-6}	0.077	2.6×10^{-4}	8.6×10^{-5}	0	8.3×10^{-6}	67	17	17	329	19	72
	34.8	0.57	9.4×10^{-6}	0.084	0.0031	0.0012	0	1.2×10^{-4}	61	15	17	314	19	85
	1491	0.26	9.7×10^{-6}	0.10	0.0015	7.0×10^{-4}	0	5.0×10^{-5}	53	14	17	325	19	88
	No	0.013	7.9×10^{-6}	0.073	0.090	0.071	0	6.6×10^{-4}	21	2.7	17	325	19	88

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters				
Spray Type =	H_c @ 42 °C (m ³ /m ³ gas)	D_1 @ 24 °C (cm ² /sec)	D_2 @ 24 °C (cm ² /sec)	C_{1in} (mg/L)	C_{1out} (mg/L)	C_{2in} (mg/L)	C_{2out} (mg/L)	η (%)	k_A (L/min)	k_gA (L/min)	k_g/k_A	Mass Closo (%)		
unknown	10	2.3	9.2×10^{-6}	0.072	9.4×10^{-5}	2.2×10^{-5}	0	4.3×10^{-5}	77	21	21	371	17	80
	42	1.6	8.5×10^{-6}	0.077	2.4×10^{-4}	7.8×10^{-5}	0	7.8×10^{-6}	68	16	17	293	17	73
	13.4	0.78	9.4×10^{-6}	0.084	0.0028	0.0010	0	1.3×10^{-4}	64	16	17	296	17	93
	34.8	0.41	9.7×10^{-6}	0.10	0.0014	6.7×10^{-4}	0	5.6×10^{-5}	52	12	14	236	17	97
	1491	0.017	7.9×10^{-6}	0.073	0.089	0.073	0	0.0010	18	3.7	16	282	17	96
	No person Present =													

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters					
Spray Type =	unknown	$H_v @ 43^\circ\text{C}$	$D_v @ 24^\circ\text{C}$	$D_g @ 24^\circ\text{C}$	$C_{g,in}$	$C_{g,out}$	$C_{g,ind}$	$C_{g,ind}$	η	$K_{f,A}$	$k_{f,A}$	$k_{f,A}$	Mass Clo		
Duration (min) =	10	Chemical	$(\text{m}^3_{\text{liq}}/\text{m}^3_{\text{gas}})$	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(L/min)	(%)		
Liquid Temperature (C) =	43	CCl_4	2.4	9.2×10^{-6}	0.072	8.1×10^{-5}	3.3×10^{-5}	0	2.0×10^{-6}	59	8.9	9.0	329	36	83
Liquid Flowrate (L/min) =	9.7	PCE	1.6	8.5×10^{-6}	0.077	1.3×10^{-4}	4.9×10^{-5}	0	3.2×10^{-6}	69	12	12	445	36	73
Gas Flowrate (L/min) =	34.8	Trichloroethene	0.79	9.4×10^{-6}	0.084	0.0018	5.5×10^{-4}	0	5.5×10^{-5}	69	13	13	483	36	83
Shower Stall Volume (L) =	1491	Chloroform	0.42	9.7×10^{-6}	0.10	0.0025	9.2×10^{-4}	0	7.5×10^{-5}	63	12	12	446	36	88
Person Present =	No	TCPA	0.017	7.9×10^{-6}	0.073	0.082	0.058	0	8.0×10^{-4}	29	4.0	10	377	36	87

STUDY: Giardinò and Andelman

Study year: 1991

Study year: 1991

Reference: Poster paper for the Annual Conference of the American Water Works Association, 1991

Reference:
Solution Method:
Method 1

Solution Method:

Assumptions:

Assumptions:
C_{gln} = 0

Comments:
All values from Little J.C. (1992) *Environmental Science and Technology*, Vol. 26, No. 7, pp. 1341-1349.

Comments:

* = Could not be determined with available data; n/m = not measured.

[illegible]

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 42\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C } D_3 @ 24\text{ C}$ (m^3/m^3)	C_{in} (mg/L)	$K_d A$ (L/min)
Duration (min) = 11		C_{out} (mg/L)	$k_d A$ (L/min)
Liquid Temperature (C) = 42		$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 5		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 52			
Shower Stall Volume (L) = 1200			
Person Present = No			

64

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 42\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C } D_3 @ 24\text{ C}$ (m^3/m^3)	C_{in} (mg/L)	$K_d A$ (L/min)
Duration (min) = 11		C_{out} (mg/L)	$k_d A$ (L/min)
Liquid Temperature (C) = 42		$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 5		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 42			
Shower Stall Volume (L) = 1200			
Person Present = No			

65

STUDY:

McKone and Knezovich

1991

Study year:

Reference: *Journal of the Air and Waste Management Association*, Vol. 41, 1991, pp. 282-286

Solution Method:

Method 1

Assumptions:

 $C_{g,in} = 0$

Comments:

Studies #66 and #67 based on 4 experiments, respectively.

 C_{out} predicted based on reported average stripping efficiency in paper.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 22\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C } D_3 @ 24\text{ C}$ (m^3/m^3)	C_{in} (mg/L)	$K_d A$ (L/min)
Duration (min) = 20		C_{out} (mg/L)	$k_d A$ (L/min)
Liquid Temperature (C) = 22		$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 9.5		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 460			
Shower Stall Volume (L) = 2300			
Person Present = No			

66

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = unknown	$H_c @ 37\text{ C } D_1 @ 24\text{ C } D_2 @ 24\text{ C } D_3 @ 24\text{ C}$ (m^3/m^3)	C_{in} (mg/L)	$K_d A$ (L/min)
Duration (min) = 20		C_{out} (mg/L)	$k_d A$ (L/min)
Liquid Temperature (C) = 37		$C_{g,in}$ (mg/L)	k_g/k_l (L/min)
Liquid Flowrate (L/min) = 9.5		$C_{g,out}$ (mg/L)	Mass Closure (%)
Gas Flowrate (L/min) = 460			
Shower Stall Volume (L) = 2300			
Person Present = No			

67

Jo, Weisel, and Lioy

1990

Study year: Risk Analysis, Vol. 10, No. 4, 1990, pp. 581-585

Reference: Method 2

Solution Method:

Assumptions: $C_{g,in} = 0$.

$Q_g = 0$.

Assumed shower air concentration increased linearly such that average gas-phase concentration of entire shower event occurred at the midpoint. Experiments were started 2 minutes after starting water through shower nozzle. Gas samples are average value of 10-minute sample collection.

Comments:

* = Could not be determined with available data; n/m = not measured.

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Spray Type =	unknown	Chemical	$H_c @ 40\text{ C}$ (m^3/m^3_{gas})	$D_l @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	Mass Closure (%)
Duration (min) =	10	Chloroform	0.37	9.7×10^{-6}	0.10	0.013	n/m	0	6.9×10^{-5}	*	2.0	*	*
Liquid Temperature (C) =	40	Chloroform	0.37	9.7×10^{-6}	0.10	0.013	n/m	0	5.8×10^{-5}	*	1.6	*	*
Liquid Flowrate (L/min) =	8.7	Chloroform	0.37	9.7×10^{-6}	0.10	0.020	n/m	0	1.2×10^{-4}	*	2.4	*	*
Gas Flowrate (L/min) =	0	Chloroform	0.37	9.7×10^{-6}	0.10	0.021	n/m	0	9.09×10^{-5}	*	1.6	*	*
Shower Stall Volume (L) =	1666	Chloroform	0.37	9.7×10^{-6}	0.10	0.023	n/m	0	9.0×10^{-5}	*	1.4	*	*
Person Present =	No	Chloroform	0.37	9.7×10^{-6}	0.10	0.024	n/m	0	1.2×10^{-4}	*	1.8	*	*
		Chloroform	0.37	9.7×10^{-6}	0.10	0.024	n/m	0	2.0×10^{-4}	*	3.4	*	*
		Chloroform	0.37	9.7×10^{-6}	0.10	0.025	n/m	0	1.7×10^{-4}	*	2.8	*	*
		Chloroform	0.37	9.7×10^{-6}	0.10	0.027	n/m	0	2.0×10^{-4}	*	2.4	*	*
		Chloroform	0.37	9.7×10^{-6}	0.10	0.028	n/m	0	2.0×10^{-4}	*	2.8	*	*
		Chloroform	0.37	9.7×10^{-6}	0.10	0.031	n/m	0	2.0×10^{-4}	*	2.5	*	*
		Chloroform	0.37	9.7×10^{-6}	0.10	0.032	n/m	0	2.3×10^{-4}	*	2.8	*	*
		Chloroform	0.37	9.7×10^{-6}	0.10	0.040	n/m	0	3.3×10^{-4}	*	3.3	*	*

68

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Spray Type =	unknown	Chemical	$H_c @ 40\text{ C}$ (m^3/m^3_{gas})	$D_l @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	Mass Closure (%)
Duration (min) =	10	Chloroform	0.37	9.7×10^{-6}	0.10	0.022	n/m	0	1.3×10^{-4}	*	2.2	*	*
Liquid Temperature (C) =	40	Chloroform	0.37	9.7×10^{-6}	0.10	0.023	n/m	0	1.2×10^{-4}	*	1.9	*	*
Liquid Flowrate (L/min) =	8.7	Chloroform	0.37	9.7×10^{-6}	0.10	0.025	n/m	0	1.3×10^{-4}	*	2.0	*	*
Gas Flowrate (L/min) =	0	Chloroform	0.37	9.7×10^{-6}	0.10	0.029	n/m	0	2.0×10^{-4}	*	2.6	*	*
Shower Stall Volume (L) =	1666	Chloroform	0.37	9.7×10^{-6}	0.10	0.029	n/m	0	2.3×10^{-4}	*	3.1	*	*
Person Present =	Yes	Chloroform	0.37	9.7×10^{-6}	0.10	0.036	n/m	0	3.1×10^{-4}	*	3.6	*	*

69

STUDY:

Study year: 1988

Reference: Giardino, Andelman, Borrazzo, and Davidson
Journal of the Air Pollution Control Association, Vol. 38, No. 3, 1988, pp. 278-280

Solution Method: Method 1

Assumptions: $C_{g,at} = 0$

$Q_g = 0$

Comments: $C_{1,at}$ is average value based on volatilization value reported in paper.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions		Chemical Properties					Chemical Concentrations				Mass Transfer Parameters				
Spray Type =	unknown	Chemical	$H_v @ 21\text{ }^{\circ}\text{C}$ ($\text{m}^3/\text{kg}/\text{m}^3$)	$D_1 @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	$D_g @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	C_{1in} (mg/L)	C_{1out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	k_A (L/min)	k_g/k_A	Mass Closure (%)	
Duration (min) =	17	SF ₆	185	1.02×10^{-3}	*	18	10	0	n/m	44	3.5	*	*	*	
Liquid Temperature (C) =	21	SF ₆	185	1.02×10^{-5}	*	8.8	5.6	0	n/m	36	2.7	*	*	*	
Liquid Flowrate (L/min) =	6.0	SF ₆	185	1.02×10^{-5}	*	18	8.5	0	n/m	52	4.4	*	*	*	
Gas Flowrate (L/min) =	0	SF ₆	185	1.02×10^{-5}	*	26	13	0	n/m	51	4.3	*	*	*	
Shower Stall Volume (L) =	1100	SF ₆	185	1.02×10^{-5}	*	24	12	0	n/m	48	3.9	*	*	*	
Person Present =	No	SF ₆	185	1.02×10^{-5}	*	15	9.2	0	n/m	39	3.0	*	*	*	
		SF ₆	185	1.02×10^{-5}	*	19	9.4	0	n/m	50	4.2	*	*	*	
		SF ₆	185	1.02×10^{-5}	*	20	11	0	n/m	45	3.6	*	*	*	

STUDY:

Study year: 1988

Reference: Hodgson, Garbesi, Sextro, and Daisey
Lawrence Berkeley Laboratory Report, Contract No. DE-AC03-76SF00098, 1988

Solution Method: Method 1

Assumptions: Assumed entire bathroom including shower stall was well mixed, such that only bathroom measurements were used to predict K_A .

Comments: For Freon-12, used Henry's law constant given in paper, remaining chemical Henry's law constants using Ashworth et al. correlations.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions		Chemical Properties				Chemical Concentrations					Mass Transfer Parameters				
Spray Type =	unknown	Chemical	$H_v @ 40^\circ C$ (m^3/m^3)	$D_1 @ 24^\circ C$ (cm^2/sec)	$D_g @ 24^\circ C$ (cm^2/sec)	C_{1in} (mg/L)	C_{1out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	k_A (L/min)	k_g/k_A	Mass Closure (%)	
Duration (min) =	10	Freon - 12	32	1.0×10^{-4}	*	0.073	0.010	4.2×10^{-6}	4.3×10^{-5}	86	27	*	*	23	
Liquid Temperature (C) =	40	Freon - 11	6.8	9.0×10^{-6}	0.084	0.011	0.0010	4.0×10^{-6}	1.1×10^{-5}	91	33	34	149	4.4	
Liquid Flowrate (L/min) =	13.7	POE	1.4	8.5×10^{-6}	0.077	0.018	0.0032	6.0×10^{-6}	2.5×10^{-5}	82	24	28	122	4.4	
Gas Flowrate (L/min) =	51	TCA	1.2	9.0×10^{-6}	0.080	0.0034	5.0×10^{-4}	1.4×10^{-6}	6.6×10^{-5}	85	27	32	140	4.4	
Bathroom Volume (L) =	10900	Trichloroethene	0.73	9.4×10^{-6}	0.084	0.0027	4.0×10^{-4}	0	n/m	85	27	35	154	4.4	
Person Present =	No													*	

72

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters				
Spray Type =	unknown	Chemical	$H_v @ 40\text{ }^{\circ}\text{C}$ (m^3/m^3)	$D_1 @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	$D_g @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	C_{1in} (mg/L)	C_{1out} (mg/L)	C_{g1in} (mg/L)	C_{gend} (mg/L)	η (%)	K_A (L/min)	k_A (L/min)	k_g/k_A (L/min)	Mass Closure (%)
Duration (min) =	10	Freon - 12	32	1.0×10^{-4}	*	0.094	0.018	6.6×10^{-6}	6.7×10^{-5}	81	23	*	*	30
Liquid Temperature (C) =	40	Freon - 11	6.8	9.0×10^{-6}	0.084	0.0094	0.0018	4.5×10^{-6}	1.2×10^{-5}	81	23	*	*	37
Liquid Flowrate (L/min) =	13.7	PCE	1.4	8.5×10^{-6}	0.077	0.029	0.0042	3.6×10^{-6}	2.2×10^{-5}	86	27	*	*	26
Gas Flowrate (L/min) =	51	TCA	1.2	9.0×10^{-6}	0.080	0.0031	8.0×10^{-4}	6.6×10^{-6}	9.6×10^{-5}	74	19	*	*	57
Bathroom Volume (L) =	10900	Trichloroethene	0.73	9.4×10^{-6}	0.084	0.0030	4.0×10^{-4}	0	n/m	87	28	*	*	*
Person Present =	Yes													*

STUDY:

Study year:

Reference:

Solution Method:

Assumptions:

Comments:

Hess, Weiffenbach, and Norton

1982

Environment International, Vol. 8, 1982, pp. 59-66

N/A

Stripping efficiency is value reported in paper. No data given to confirm.

Stripping efficiency based on four measurements.

Not enough data collected to calculate K_LA or mass closure.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = Duration (min) = Liquid Temperature (C) = Liquid Flowrate (L/min) = Gas Flowrate (L/min) = Bathroom Volume (L) = Person Present =	unknown not given Chemical Radon $H_c @ 25\text{ C}$ ($\text{m}^3/\text{m}^3_{\text{gas}}$) $D_1 @ 24\text{ C}$ (cm^2/sec) $D_2 @ 24\text{ C}$ (cm^2/sec) 4.4 5.2×10^{-6}	C_{in} (mg/L) C_{out} (mg/L) $C_{\text{g,in}}$ (mg/L) $C_{\text{g,end}}$ (mg/L)	η (%) K_LA (L/min) k_gA (L/min) k_g/k_l Mass Closure (%)
			65

73

STUDY:

Study year:

Reference:

Solution Method:

Assumptions:

Comments:

Gesell and Pritchard

1980

In *Natural Radiation Environment III*, Vol. 2, Houston: Technical Information Center, U.S. Department of Energy, pp. 1347-1363

N/A

Stripping efficiency is value reported in paper. No data given to confirm.

Liquid-phase diffusion coefficient estimated using relationship given for Giordano and Hageman (1996)

Not enough data collected to calculate K_LA or mass closure.

* = Could not be determined with available data; n/m = not measured.

Operating Conditions	Chemical Properties	Chemical Concentrations	Mass Transfer Parameters
Spray Type = Duration (min) = Liquid Temperature (C) = Liquid Flowrate (L/min) = Gas Flowrate (L/min) = Bathroom Volume (L) = Person Present =	unknown not given Chemical Radon $H_c @ 25\text{ C}$ ($\text{m}^3/\text{m}^3_{\text{gas}}$) $D_1 @ 24\text{ C}$ (cm^2/sec) $D_2 @ 24\text{ C}$ (cm^2/sec) 4.4 5.2×10^{-6}	C_{in} (mg/L) C_{out} (mg/L) $C_{\text{g,in}}$ (mg/L) $C_{\text{g,end}}$ (mg/L)	η (%) K_LA (L/min) k_gA (L/min) k_g/k_l Mass Closure (%)
			65

74

STUDY:

Partridge, Horton, and Sensintaifer

1979

Reference:Data in Nazaroff *et al.*, *Health Physics*, Vol. 52, No. 3, 1987, pp. 281-295**Solution Method:**

N/A

Assumptions:

Stripping efficiency is value reported in paper. No data given to confirm.

Liquid-phase diffusion coefficient estimated using relationship given for Giordano and Hageman (1996).

Comments:Not enough data collected to calculate K_A or mass closure.

* = Could not be determined with available data; n/m = not measured.

75

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters					
Spray Type =	unknown	Chemical	$H_c @ 25\text{ }^{\circ}\text{C}$ ($\text{m}^3/\text{kg}/\text{m}^3_{\text{gas}}$)	$D_l @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	$D_g @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	$k_g A$ (L/min)	k_g/k_l (L/min)	Mass Closure (%)
Duration (min) =	not given	Radon	4.4	5.2×10^{-3}	*	*	*	*	71	*	*	*	*
Liquid Temperature (C) =	n/m												
Liquid Flowrate (L/min) =	n/m												
Gas Flowrate (L/min) =	n/m												
Bathroom Volume (L) =	n/m												
Person Present =	No												

BATHTUB DATABASE

STUDY: Howard, C.
 1998
 Reference: Volatilization Rates of Chemicals from Drinking Water to Indoor Air. Ph.D. Dissertation. University of Texas at Austin, May 1988
 Solution Methods: Method 1 for ethyl acetate, toluene, ethylbenzene, cyclohexane
 Method 2 for acetone
 Assumptions: None
 Comments: Values of η and K_A are averages of values determined for three separate time periods within experiment.
 * = Could not be determined with available data.

Entry # 1

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Operation =	Flow-through	$H_b @ 22\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)		C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	k_g/k_l (L/min)	Mass Closure (%)
Duration (min) =	8	Chemical											
Liquid Temperature (C) =	22	Acetone	0.0011	1.1×10^{-5}	0.11	52	50	0	0.019	3.8	0.11	2.9	37
Liquid Flowrate (L/min) =	9.1	Ethyl Acetate	0.0044	9.5×10^{-6}	0.092	25	24	0	0.028	6.1	0.64	4.5	168
Gas Flowrate (L/min) =	355	Toluene	0.25	9.1×10^{-6}	0.085	4.9	3.6	0	0.019	26	2.9	3.2	117
Shower Stall/Bath Volume (L) =	1745	Ethylbenzene	0.28	8.4×10^{-6}	0.077	3.9	2.9	0	0.012	27	2.9	3.1	117
Person Present =	No	Cyclohexane	6.7	9.0×10^{-6}	0.088	0.94	0.68	0	0.0031	28	3.1	3.1	115
													37
													85

2

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Operation =	Flow-through	$H_b @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)		C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	k_g/k_l (L/min)	Mass Closure (%)
Duration (min) =	8	Chemical											
Liquid Temperature (C) =	23	Acetone	0.0011	1.1×10^{-5}	0.11	40	39	0	0.016	3.1	0.15	3.2	136
Liquid Flowrate (L/min) =	9.1	Ethyl Acetate	0.0046	9.5×10^{-6}	0.092	25	23	0	0.027	4.7	0.49	3.0	126
Gas Flowrate (L/min) =	345	Toluene	0.26	9.1×10^{-6}	0.085	6.4	4.9	0	0.019	24	2.4	2.6	111
Shower Stall/Bath Volume (L) =	1745	Ethylbenzene	0.30	8.4×10^{-6}	0.077	4.9	3.8	0	0.0088	24	2.4	2.6	109
Person Present =	No	Cyclohexane	6.9	9.0×10^{-6}	0.088	1.4	1.0	0	0.0032	29	2.9	2.9	126
													43
													88

3

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Operation =	Flow-through	$H_b @ 36\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)		C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	k_g/k_l (L/min)	Mass Closure (%)
Duration (min) =	8	Chemical											
Liquid Temperature (C) =	36	Acetone	0.0024	1.1×10^{-5}	0.11	39	37	0	0.036	5.3	0.54	6.0	249
Liquid Flowrate (L/min) =	9.1	Ethyl Acetate	0.0080	9.5×10^{-6}	0.092	24	21	0	0.059	11	1.2	4.9	205
Gas Flowrate (L/min) =	359	Toluene	0.38	9.1×10^{-6}	0.085	6.7	4.1	0	0.037	38	4.5	4.8	198
Shower Stall/Bath Volume (L) =	1745	Ethylbenzene	0.58	8.4×10^{-6}	0.077	5.9	3.6	0	0.022	39	4.5	4.7	196
Person Present =	No	Cyclohexane	10	9.0×10^{-6}	0.088	2.3	1.3	0	0.0074	38	5.1	5.1	211
													42
													82

4

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Operation =	Flow-through	$H_b @ 25\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)		C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	k_g/k_l (L/min)	Mass Closure (%)
Duration (min) =	8	Chemical											
Liquid Temperature (C) =	25	Acetone	0.0013	1.1×10^{-5}	0.11	40	40	0	0.017	1.7	0.18	2.4	159
Liquid Flowrate (L/min) =	6.1	Ethyl Acetate	0.0050	9.5×10^{-6}	0.092	25	24	0	0.029	4.5	0.32	1.3	86
Gas Flowrate (L/min) =	350	Toluene	0.27	9.1×10^{-6}	0.085	5.2	4.0	0	0.013	22	1.6	1.7	110
Shower Stall/Bath Volume (L) =	1745	Ethylbenzene	0.32	8.4×10^{-6}	0.077	4.0	3.1	0	0.0077	22	1.5	1.6	106
Person Present =	No	Cyclohexane	7.2	9.0×10^{-6}	0.088	1.1	0.81	0	0.0029	22	1.7	1.7	110
													66
													96

Operating Conditions		Chemical Properties					Chemical Concentrations				Mass Transfer Parameters					
Operation =	Flow-through	H _c @ 36 C (m ³ /m ³ gas)	D _l @ 24 C (cm ² /sec)	D _g @ 24 C (cm ² /sec)	C _{g,in} (mg/L)	C _{g,out} (mg/L)	C _{l,in} (mg/L)	C _{l,out} (mg/L)	C _{g,end} (mg/L)	η (%)	k _f A (L/min)	k _g A (L/min)	k _g /k _l	Mass Closure (%)		
Duration (min) =	8	Chemical														
Liquid Temperature (C) =	36	Acetone	0.0024	1.1 x 10 ⁻⁵	0.11		48	46	0	0.034	4.3	0.43	2.4	227	96	101
Liquid Flowrate (L/min) =	6.1	Ethyl Acetate	0.0080	9.5 x 10 ⁻⁶	0.092		25	22	0	0.043	14	1.1	2.4	234	96	101
Gas Flowrate (L/min) =	361	Toluene	0.38	9.1 x 10 ⁻⁶	0.085		6.0	4.2	0	0.023	30	2.2	2.2	214	96	107
Shower Stall/Bathtub Volume (L) =	1745	Ethylbenzene	0.58	8.4 x 10 ⁻⁶	0.077		4.0	3.1	0	0.017	29	2.1	2.2	207	96	100
Person Present =	No	Cyclohexane	10	9.0 x 10 ⁻⁶	0.088		1.1	0.77	0	0.0038	27	1.9	1.9	182	96	103

Operating Conditions		Chemical Properties					Chemical Concentrations				Mass Transfer Parameters				
Operation =	Flow-through	Chemical	$H_c @ 37\text{ C}$ ($\text{m}^3/\text{kg}/\text{m}^3_{\text{gas}}$)	$D_l @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	k_dA (L/min)	k_d/k_l (L/min)	Mass Closure (%)		
Duration (min) =	8	Acetone	0.0025	1.1×10^{-5}	0.11	40	38	0	0.033	4.8	0.46	4.2	211	50	101
Liquid Temperature (C) =	37	Ethyl Acetate	0.0084	9.5×10^{-6}	0.092	23	21	0	0.049	10	0.79	2.7	135	50	105
Liquid Flowrate (L/min) =	6.1	Toluene	0.39	9.1×10^{-6}	0.085	6.0	3.7	0	0.023	38	2.9	3.1	152	50	92
Gas Flowrate (L/min) =	365	Ethylbenzene	0.59	8.4×10^{-6}	0.077	5.9	3.7	0	0.015	38	2.9	3.0	151	50	85
Shower Stall/Bathtub Volume (L) =	1745	Cyclohexane	11	9.0×10^{-6}	0.088	2.0	1.2	0	0.0038	41	3.2	3.2	161	50	85
Person Present =	No														

STUDY:
Howard, C.L.

Study year:
1998

Reference:
Volatilization Rates of Chemicals from Drinking Water to Indoor Air, Ph.D. Dissertation, University of Texas at Austin, May 1988

Solution Methods:
Method 3

Assumptions:
None

Comments:
None

* = Could not be determined with available data.

Operating Conditions		Chemical Properties					Chemical Concentrations				Mass Transfer Parameters				
Operation =	Fill	Chemical	$H_c @ 24\text{ C}$ ($\text{m}^3/\text{kg}/\text{m}^3_{\text{gas}}$)	$D_l @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	k_dA (L/min)	k_d/k_l (L/min)	k_g/k_l (L/min)	Mass Closure (%)	
Duration (min) =	8														
Liquid Temperature (C) =	24	Acetone	0.0012	1.1×10^{-5}	0.11	41	39	0	0.018	4.9	0.45	7.1	395	56	97
Liquid Flowrate (L/min) =	9.1	Ethyl Acetate	0.0013	9.5×10^{-6}	0.092	25	24	0	0.030	3.0	1.0	4.9	274	56	103
Final Liquid Volume (L) =	73	Toluene	0.27	9.1×10^{-6}	0.085	8.0	5.6	0	0.029	31	4.1	4.4	244	56	89
Gas Flowrate (L/min) =	373	Ethylbenzene	0.31	8.4×10^{-6}	0.077	9.8	6.7	0	0.020	33	4.4	4.6	257	56	82
Shower Stall/Bathtub Volume (L) =	1745	Cyclohexane	7.1	9.0×10^{-6}	0.088	3.1	1.8	0	0.0063	46	7.1	7.1	396	56	73

Operating Conditions		Chemical Properties					Chemical Concentrations				Mass Transfer Parameters				
Operation =	Fill	$H_c @ 35\text{ C}$ ($\text{m}^3/\text{kg}/\text{m}^3_{\text{gas}}$)	$D_l @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_dA (L/min)	k_d/k_l (L/min)	Mass Closure (%)			
Duration (min) =	8	Chemical													
Liquid Temperature (C) =	35	Acetone	0.0022	1.1×10^{-5}	0.11	43	40	0	0.031	5.2	0.53	9.3	253	27	98
Liquid Flowrate (L/min) =	9.1	Ethyl Acetate	0.0077	9.5×10^{-6}	0.092	24	23	0	0.045	5.3	1.4	8.3	228	27	106
Final Liquid Volume (L) =	73	Toluene	0.36	9.1×10^{-6}	0.085	6.2	4.0	0	0.036	30	5.3	5.8	159	27	93
Gas Flowrate (L/min) =	379	Ethylbenzene	0.54	8.4×10^{-6}	0.077	6.3	3.9	0	0.024	32	5.9	6.3	172	27	81
Shower Stall/Bathtub Volume (L) =	1745	Cyclohexane	10	9.0×10^{-6}	0.088	2.0	0.85	0	0.0074	47	11	11	311	27	68

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters						
Operation =	Fill	H_e @ 35 C (m^3/m^3_{gas})	D_l @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	η (%)	$k_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L	Mass Closure (%)		
Duration (min) =	8	0.0024	1.1×10^{-5}	0.11	40	39	0	0.032	2.0	0.64	5.9	303	51	101
Liquid Temperature (C) =	36	0.0080	9.5×10^{-6}	0.092	23	22	0	0.044	3.1	1.5	5.3	269	51	107
Liquid Flowrate (L/min) =	9.1	0.38	9.1×10^{-6}	0.085	6.3	4.5	0	0.037	31	3.7	3.8	193	51	101
Final Liquid Volume (L) =	73	0.58	8.4×10^{-6}	0.077	5.4	3.8	0	0.024	32	3.8	4.0	202	51	93
Gas Flowrate (L/min) =	373	10	9.0×10^{-6}	0.088	1.2	0.66	0	0.0074	46	7.4	7.4	376	51	87
Shower Stall/Bathtub Volume (L) =	1745													

9

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters					
Operation =	Fill	H_e @ 23 C (m^3/m^3_{gas})	D_l @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L	Mass Closure		
Duration (min) =	12	0.0011	1.1×10^{-5}	0.11	41	39	0	0.019	5.8	0.39	4.7	365	77	96
Liquid Temperature (C) =	23	0.0046	9.5×10^{-6}	0.092	26	25	0	0.032	3.1	0.71	2.7	208	77	104
Liquid Flowrate (L/min) =	6.1	0.26	9.1×10^{-6}	0.085	6.8	4.9	0	0.034	29	2.6	2.7	208	77	101
Final Liquid Volume (L) =	73	0.30	8.4×10^{-6}	0.077	7.3	5.1	0	0.023	31	2.7	2.8	220	77	88
Gas Flowrate (L/min) =	370	6.9	9.0×10^{-6}	0.088	3.0	1.8	0	0.0078	43	4.4	4.4	344	77	84
Shower Stall/Bathtub Volume (L) =	1745													

10

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters					
Operation =	Fill	H_e @ 35 C ($m^3_{\text{air}}/m^3_{\text{gas}}$)	D_l @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L	Mass Closure (%)	
Duration (min) =	11.4	Chemical												
Liquid Temperature (C) =	35	Acetone	0.0022	1.1×10^{-5}	0.11	40	37	0	0.032	7.7	0.39	4.2	191	46
Liquid Flowrate (L/min) =	6.1	Ethyl Acetate	0.0077	9.5×10^{-6}	0.092	23	22	0	0.047	7.0	1.0	3.8	175	46
Final Liquid Volume (L) =	69	Toluene	0.37	9.1×10^{-6}	0.085	5.0	3.5	0	0.026	30	2.7	2.8	129	46
Gas Flowrate (L/min) =	377	Ethylbenzene	0.56	8.4×10^{-6}	0.077	4.2	3.0	0	0.015	29	2.5	2.6	121	46
Shower Stall/Bathtub Volume (L) =	1745	Cyclohexane	10	9.0×10^{-6}	0.088	1.2	0.63	0	0.0041	46	5.4	5.4	245	46

11

STUDY: Howard, C.L.

Study year: 1998

Reference: Volatilization Rates of Chemicals from Drinking Water to Indoor Air. Ph.D. Dissertation. University of Texas at Austin, May 1988

Solution Methods: Method 4 for toluene, ethylbenzene, and cyclohexane

Method 5 for acetone and ethyl acetate

Assumptions: None

Comments: Stripping efficiencies for entries 12 - 14 based on gas-phase data.

* = Could not be determined with available data.

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Operation =	Bathing	H_e @ 23 C (m^3/m^3_{gas})	D_l @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L	Mass Closure
Duration (min) =	20	0.0011	1.1×10^{-5}	0.11	40	39	0.021	0.0030	0.6	*	*	99
Liquid Temperature (C) =	23	0.0046	9.5×10^{-6}	0.092	25	25	0.035	0.0023	1.6	*	*	100
Liquid Volume (L) =	73	0.26	9.1×10^{-6}	0.085	4.9	5.1	0.037×10^7	7.9	*	*	*	96
Gas Flowrate (L/min) =	370	0.3	8.4×10^{-6}	0.077	5.1	5.3	0.025×10^7	5.1	*	*	*	100
Shower Stall/Bathtub Volume (L) =	1745	6.9	9.0×10^{-6}	0.088	1.8	1.9	0.009	0	4.7	*	*	99
Person Present =	No											

12

KITCHEN SINK DATABASE

STUDY:

Howard and Corsi

Study year:

1996

Reference:

Journal of the Air and Waste Management Association, Vol. 46, 1996, pp. 830-837.

Solution Method:

Method 6

Assumptions:

 C_g assumed to be negligible $C_{g,in} = 0$

Comments:

Mass transfer values based on recirculating flow.

* = Could not be determined with available data.

Entry #
1

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Aerator Type =	None	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$D_3 @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	Mass Closure (%)
Liquid Temperature (C) =	23	Chemical	0.0011	1.1×10^{-5}	0.11	93	45	0	4.9	0.24	1.3	104
Liquid Flowrate (L/min) =	4.8	Acetone	0.26	9.1×10^{-6}	0.085	11	0.44	0	21	1.0	1.0	104
Hydraulic Residence Time (min) =	10	Toluene	6.9	9.0×10^{-6}	0.088	7.2	0.18	0	24	1.2	1.2	104
Dishes =	None	Cyclohexane										

2

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Aerator Type =	None	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$D_3 @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	Mass Closure (%)
Liquid Temperature (C) =	23	Chemical	0.0011	1.1×10^{-5}	0.11	56	41	0	2.2	0.17	1.7	88
Liquid Flowrate (L/min) =	7.9	Acetone	0.26	9.1×10^{-6}	0.085	14	1.2	0	17	1.3	1.4	72
Hydraulic Residence Time (min) =	6.3	Toluene	6.9	9.0×10^{-6}	0.088	12	0.74	0	19	1.5	1.5	77
Dishes =	None	Cyclohexane										

3

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Aerator Type =	Screen	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$D_3 @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	Mass Closure (%)
Liquid Temperature (C) =	23	Chemical	0.0011	1.1×10^{-5}	0.11	70	53	0	1.7	0.080	1.0	41
Liquid Flowrate (L/min) =	4.8	Acetone	0.26	9.1×10^{-6}	0.085	9.4	0.84	0	13	0.65	0.7	30
Hydraulic Residence Time (min) =	10	Toluene	6.9	9.0×10^{-6}	0.088	7.7	0.30	0	19	0.90	0.9	38
Dishes =	None	Cyclohexane										

4

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Aerator Type =	Screen	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$D_3 @ 24\text{ C}$ (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	Mass Closure (%)
Liquid Temperature (C) =	23	Chemical	0.0011	1.1×10^{-5}	0.11	58	49	0	1.1	0.090	1.6	44
Liquid Flowrate (L/min) =	7.9	Acetone	0.26	9.1×10^{-6}	0.085	12	1.5	0	14	1.2	1.4	37
Hydraulic Residence Time (min) =	6.3	Toluene	6.9	9.0×10^{-6}	0.088	8.4	0.64	0	18	1.4	1.4	38
Dishes =	None	Cyclohexane										

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Aerator Type =	Bubble Aerator	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$C_{1,\text{in}}$ (mg/L)	$C_{1,\text{out}}$ (mg/L)	$C_{2,\text{in}}$ (mg/L)	$K_L A$ (L/min)	$k_p A$ (L/min)	k_p/k_L (%)	Mass Closure (%)
Liquid Temperature (C) =	23										
Liquid Flowrate (L/min) =	4.8										
Hydraulic Residence Time (min) =	10										
Dishes =	None										

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Aerator Type =	Bubble Aerator	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$C_{1,\text{in}}$ (mg/L)	$C_{1,\text{out}}$ (mg/L)	$C_{2,\text{in}}$ (mg/L)	$K_L A$ (L/min)	$k_p A$ (L/min)	k_p/k_L (%)	Mass Closure (%)
Liquid Temperature (C) =	23										
Liquid Flowrate (L/min) =	6.3										
Hydraulic Residence Time (min) =	8.1										
Dishes =	None										

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Aerator Type =	Bubble Aerator	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$C_{1,\text{in}}$ (mg/L)	$C_{1,\text{out}}$ (mg/L)	$C_{2,\text{in}}$ (mg/L)	$K_L A$ (L/min)	$k_p A$ (L/min)	k_p/k_L (%)	Mass Closure (%)
Liquid Temperature (C) =	23										
Liquid Flowrate (L/min) =	7.9										
Hydraulic Residence Time (min) =	6.3										
Dishes =	None										

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Aerator Type =	Bubble Aerator	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$C_{1,\text{in}}$ (mg/L)	$C_{1,\text{out}}$ (mg/L)	$C_{2,\text{in}}$ (mg/L)	$K_L A$ (L/min)	$k_p A$ (L/min)	k_p/k_L (%)	Mass Closure (%)
Liquid Temperature (C) =	23										
Liquid Flowrate (L/min) =	4.8										
Hydraulic Residence Time (min) =	10										
Dishes =	Yes										

Operating Conditions		Chemical Properties		Chemical Concentrations				Mass Transfer Parameters			
Aerator Type =	Bubble Aerator	$H_c @ 23\text{ C}$ (m^3/m^3)	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_2 @ 24\text{ C}$ (cm^2/sec)	$C_{1,\text{in}}$ (mg/L)	$C_{1,\text{out}}$ (mg/L)	$C_{2,\text{in}}$ (mg/L)	$K_L A$ (L/min)	$k_p A$ (L/min)	k_p/k_L (%)	Mass Closure (%)
Liquid Temperature (C) =	23										
Liquid Flowrate (L/min) =	6.3										
Hydraulic Residence Time (min) =	8.1										
Dishes =	Yes										

STUDY: Wooley, Nazaroiff, and Hodgson

Study year: 1990

Reference: *Journal of the Air and Waste Management Association*, Vol. 40, 1990, pp.1114-1120

Solution Method: Method 8

Assumptions: Only significant mass transfer occurring due to wash solution with added ethanol.

Comments: There is not enough information given to consider additional emissions due to rinsing of dishes.

Mass closure values based on numbers given in paper.

* = Could not be determined with available data.

10

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Aerator Type =	unknown	H _c @ 23 C (m ³ /m ³ gas)	D _i @ 24 C (cm ² /sec)	D _g @ 24 C (cm ² /sec)	C _i (mg/L)	C _i (mg/L)	C _g (mg/L)	C _g (mg/L)	η (%)	K _L A (L/min)	k _g A (L/min)	k _g /k _i	Mass Closure (%)
Liquid Temperature (C) =	43												
Liquid Volume (L) =	7.6	0.0012	1.3 x 10 ⁻⁵	0.12	113	101	0	0	11	0.084	*	*	94
Duration (min) =	10	0.0012	1.3 x 10 ⁻⁵	0.12	113	105	0	0	7.1	0.055	*	*	96
Dishes =	Yes	0.0012	1.3 x 10 ⁻⁵	0.12	113	99	0	0	12	0.10	*	*	92

11

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Aerator Type =	unknown	H _c @ 23 C (m ³ /m ³ gas)	D _i @ 24 C (cm ² /sec)	D _g @ 24 C (cm ² /sec)	C _i (mg/L)	C _i (mg/L)	C _g (mg/L)	C _g (mg/L)	η (%)	K _L A (L/min)	k _g A (L/min)	k _g /k _i	Mass Closure (%)
Liquid Temperature (C) =	55												
Liquid Volume (L) =	7.6	*	1.3 x 10 ⁻⁵	0.12	278	279	0	0	-0.4	-5.1 x 10 ⁻⁴	*	*	106
Duration (min) =	70	*	1.3 x 10 ⁻⁵	0.12	278	283	0	0	-1.8	-0.0020	*	*	106
Dishes =	Yes	*	1.3 x 10 ⁻⁵	0.12	278	278	0	0	0	0	*	*	105

WASHING MACHINE DATABASE

STUDY:

Howard, C.L.

Study year:

1998

Reference:

Journal of the Air and Waste Management Association, Vol. 48, p. 907

Solution Method:

Method 3

Assumptions:

None

Comments:

One gas sample collected for duration of experiment and one gas sample collected at end of experiment.
Values of k_g/k_i based solely on toluene, ethylbenzene, and cyclohexane data.

* = Could not be determined with available data.

Entry #
1

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Cycle Type =	fill for rinse	H_c @ 19 C (m^3/m^3)	D_1 @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_i Mass Closure (%)
Duration (min) =	3.3	Chemical			55	55	0	0.042	2.1	0.23	*	*
Liquid Temperature (C) =	19	Acetone	0.00089	1.1×10^{-5}	0.11				9.8	1.8	2.9	21
Liquid Flowrate (L/min) =	14.6	Toluene	0.22	9.1×10^{-6}	0.085	7.5	6.8	0	9.8	1.8	2.9	21
Gas Flowrate (L/min) =	55	Ethylbenzene	0.23	8.4×10^{-6}	0.077	6.7	6.0	0	9.5	1.7	2.8	20
Final Headspace Volume (L) =	101	Cyclohexane	6.0	9.0×10^{-6}	0.088	2.5	2.1	0	15	2.8	2.9	21
Clothes Present =	no											

2

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Cycle Type =	fill for rinse	H_c @ 21 C (m^3/m^3)	D_l @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	C_{lin} (mg/L)	C_{lout} (mg/L)	C_{gin} (mg/L)	C_{gend} (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_l Mass Closure (%)
Duration (min) =	3.3	Chemical			55	55	0	0.067	1	*	*	*
Liquid Temperature (C) =	21	Acetone	0.0010	1.1×10^{-5}	0.11				13	2.8	5.4	25
Liquid Flowrate (L/min) =	13.7	Toluene	0.24	9.1×10^{-6}	0.085	8.5	7.3	0	13	2.8	5.4	25
Gas Flowrate (L/min) =	55	Ethylbenzene	0.27	8.4×10^{-6}	0.077	7.3	6.3	0	13	2.9	5.3	24
Final Headspace Volume (L) =	104	Cyclohexane	6.0	9.0×10^{-6}	0.088	2.1	1.6	0	25	5.3	5.5	25
Clothes Present =	no											

3

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Cycle Type =	fill for wash	H_c @ 19 C (m^3/m^3)	D_l @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	C_{lin} (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$k_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L Mass Closure (%)
Duration (min) =	3.3	Chemical			53	53	0	0.061	0.7	*	*	*
Liquid Temperature (C) =	19	Acetone	0.00089	1.1×10^{-5}	0.11				13	4.2	7.0	47
Liquid Flowrate (L/min) =	13.8	Toluene	0.23	9.1×10^{-6}	0.085	7.9	6.3	0	16	5.0	8.1	54
Gas Flowrate (L/min) =	55	Ethylbenzene	0.24	8.4×10^{-6}	0.077	7.3	5.7	0	26	7.5	7.6	51
Final Headspace Volume (L) =	104	Cyclohexane	6.0	9.0×10^{-6}	0.088	2.3	1.5	0				
Clothes Present =	no											

4

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters				
Cycle Type =	fill for rinse	Chemical	H_c @ 21 C (m^3/m^3)	D_1 @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	$C_{l,in}$ (mg/L)	$C_{l,out}$ (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_i Mass Closure (%)
Duration (min) =	3.3	Chemical				56	54	0	0.038	3.0	0.086	*	*
Liquid Temperature (C) =	21	Acetone	0.0010	1.1×10^{-5}	0.11					8.2	1.5	*	*
Liquid Flowrate (L/min) =	13.7	Toluene	0.27	9.1×10^{-6}	0.085	8.6	7.8	0	0.14	10	1.9	*	*
Gas Flowrate (L/min) =	55	Ethylbenzene	0.35	8.4×10^{-6}	0.077	6.9	6.2	0	0.076	6.9	1.2	*	*
Final Headspace Volume (L) =	93	Cyclohexane	6.5	9.0×10^{-6}	0.088	2.0	1.9	0	0.028				
Clothes Present =	yes												

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	fill for rinse	H_c @ 49 C	D_l @ 24 C	D_g @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	$K_L A$	$k_g A$	k_g/k_L	Mass Closure (%)
Duration (min) =	3.3	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(L/min)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	49	0.0046	1.1×10^{-6}	0.11	0.11	52	51	0	0.053	1.2	0.19	*	101
Liquid Flowrate (L/min) =	13.6	0.54	9.1×10^{-6}	0.085	0.085	6.9	5.1	0	0.047	22	5.0	5.5	117
Gas Flowrate (L/min) =	160	1.1	8.4×10^{-6}	0.077	0.077	6.3	4.8	0	0.032	20	4.7	4.9	103
Final Headspace Volume (L) =	104	15	9.0×10^{-6}	0.088	0.088	1.7	1.2	0	0.022	28	5.4	5.4	96
Clothes Present =	no												

5

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	fill for rinse	H_c @ 47 C	D_l @ 24 C	D_g @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	$K_L A$	$k_g A$	k_g/k_L	Mass Closure (%)
Duration (min) =	3.3	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(L/min)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	47	0.0041	1.1×10^{-6}	0.11	0.11	54	52	0	0.057	2.3	0.22	*	99
Liquid Flowrate (L/min) =	13.8	0.51	9.1×10^{-6}	0.085	0.085	8.0	5.1	0	0.048	35	8.4	12	94
Gas Flowrate (L/min) =	160	0.95	8.4×10^{-6}	0.077	0.077	6.3	4.0	0	0.028	36	8.4	10	84
Final Headspace Volume (L) =	104	14	9.0×10^{-6}	0.088	0.088	2.1	1.2	0	0.073	45	11	11	69
Clothes Present =	no												

6

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	fill for rinse	H_c @ 20 C	D_l @ 24 C	D_g @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	$K_L A$	$k_g A$	k_g/k_L	Mass Closure (%)
Duration (min) =	6.5	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(L/min)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	20	0.00095	1.1×10^{-6}	0.11	0.11	55	54	0	0.026	1.8	0.038	*	102
Liquid Flowrate (L/min) =	13.7	0.24	9.1×10^{-6}	0.085	0.085	6.6	5.7	0	0.21	17	2.5	4.6	110
Gas Flowrate (L/min) =	55	0.26	8.4×10^{-6}	0.077	0.077	5.6	4.8	0	0.13	19	2.8	5.0	101
Final Headspace Volume (L) =	61	6.3	9.0×10^{-6}	0.088	0.088	1.5	1.1	0	0.048	33	4.8	4.9	93
Clothes Present =	no												

7

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	fill for rinse	H_c @ 21 C	D_l @ 24 C	D_g @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	$K_L A$	$k_g A$	k_g/k_L	Mass Closure (%)
Duration (min) =	4.75	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(L/min)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	21	0.0010	1.1×10^{-6}	0.11	0.11	51	50	0	0.036	1.2	0.12	*	99
Liquid Flowrate (L/min) =	8.6	0.24	9.1×10^{-6}	0.085	0.085	6.4	4.6	0	0.11	23	4.2	6.3	90
Gas Flowrate (L/min) =	55	0.26	8.4×10^{-6}	0.077	0.077	5.2	3.7	0	0.068	24	4.4	6.4	84
Final Headspace Volume (L) =	109	6.4	9.0×10^{-6}	0.088	0.088	1.6	0.96	0	0.022	37	6.4	6.5	72
Clothes Present =	no												

8

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	fill for rinse	H_c @ 19 C	D_l @ 24 C	D_g @ 24 C	D_g @ 24 C	$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,out}$	$K_L A$	$k_g A$	k_g/k_L	Mass Closure (%)
Duration (min) =	4.75	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(L/min)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	19	0.00089	1.1×10^{-6}	0.11	0.11	49	47	0	0.042	3.0	1.2	*	96
Liquid Flowrate (L/min) =	8.5	0.23	9.1×10^{-6}	0.085	0.085	7.4	5.8	0	0.18	9.7	3.5	4.3	98
Gas Flowrate (L/min) =	55	0.23	8.4×10^{-6}	0.077	0.077	5.9	4.6	0	0.086	9.4	3.7	4.5	91
Final Headspace Volume (L) =	110	6.0	9.0×10^{-6}	0.088	0.088	1.9	1.4	0	0.043	12	4.5	4.5	86
Clothes Present =	no												

9

Howard, C.L.

STUDY:

Study year:

Reference:

Solution Method:

Assumptions:

Comments:

1998

Volatilization Rates of Chemicals from Drinking Water to Indoor Air: Ph.D. Dissertation. University of Texas at Austin, May 1988

Method 4 for toluene, ethylbenzene, and cyclohexane.

Method 5 for acetone and ethyl acetate.

None

* = Could not be determined with available data.

10

Operating Conditions		Chemical Properties					Chemical Concentrations				Mass Transfer Parameters				
Cycle Type =	Rinse	Chemical	$H_c @ 24 C$ (m^3_{liq}/m^3_{gas})	$D_1 @ 24 C$ (cm^2/sec)	$D_g @ 24 C$ (cm^2/sec)	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$	η (L/min)	K_A (L/min)	k_A (L/min)	k_g/k_l	Mass Closure (%)	
Duration (min) =	10	Acetone	0.0012	1.1×10^{-5}	0.11	36	34	0.013	0.026	7.1	0.069	40	57	1.4	98
Liquid Temperature (C) =	24	Ethyl Acetate	0.0048	9.5×10^{-6}	0.092	23	22	0.01	0.047	12	0.15	23	32	1.4	106
Liquid Volume (L) =	47	Toluene	0.26	9.1×10^{-6}	0.085	5.1	1.4	0.0033	0.091	72	9.4	34	49	1.4	70
Gas Flowrate (L/min) =	53	Ethylbenzene	0.31	8.4×10^{-6}	0.077	4.1	0.96	0.0024	0.056	76	10	34	49	1.4	75
Final Headspace Volume (L) =	103	Cyclohexane	7.1	9.0×10^{-6}	0.088	1.4	0.012	0.0019	0.0038	99	24	26	37	1.4	28
Agitation Speed =	slow														
Clothes Present =	no														

11

Operating Conditions		Chemical Properties					Chemical Concentrations				Mass Transfer Parameters				
Cycle Type =	Rinse	Chemical	$H_c @ 22\text{ }^{\circ}\text{C}$ ($\text{m}^3/\text{m}^3_{\text{gas}}$)	$D_1 @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	$D_g @ 24\text{ }^{\circ}\text{C}$ (cm^2/sec)	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{\text{g,lin}}$ (mg/L)	$C_{\text{g,end}}$	η (%)	K_A (L/min)	k_A (L/min)	k_g/k_l	Mass Closure (%)	
Duration (min) =	10	Acetone	0.0011	1.1×10^{-5}	0.11	44	37	0.013	0.025	15	0.024	30	22	0.74	95
Liquid Temperature ($^{\circ}\text{C}$) =	22	Ethyl Acetate	0.0044	9.5×10^{-6}	0.092	27	25	0.013	0.057	8.1	0.073	23	17	0.74	103
Liquid Volume (L) =	49	Toluene	0.25	9.1×10^{-6}	0.085	7.1	2.5	0.0042	0.19	65	7.1	46	34	0.74	63
Gas Flowrate (L/min) =	53	Ethylbenzene	0.28	8.4×10^{-6}	0.077	7.1	2.2	0.0033	0.13	69	8.1	47	35	0.74	53
Final Headspace Volume (L) =	101	Cyclohexane	6.7	9.0×10^{-6}	0.088	3.6	0.028	0.013	0.019	99	23	27	20	0.74	42
Agitation Speed =	slow														
Clothes Present =	no														

12

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters					
Cycle Type =	Rinse	Chemical	$H_c @ 49\text{ C}$ (m^3/m^3_{gas})	$D_1 @ 24\text{ C}$ (cm^2/sec)	$D_g @ 24\text{ C}$ (cm^2/sec)	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,lin}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L	Mass Closure (%)	
Duration (min) =	10	Acetone	0.0046	1.1×10^{-5}	0.11	48	31	0.024	0.029	36	0.30	62	67	1.1	104
Liquid Temperature (C) =	49	Ethyl Acetate	0.014	9.5×10^{-6}	0.092	28	15	0.014	0.032	48	0.61	41	45	1.1	114
Liquid Volume (L) =	48	Toluene	0.53	9.1×10^{-6}	0.085	8.0	0.38	0.0035	0.0061	95	15	41	44	1.1	112
Gas Flowrate (L/min) =	200	Ethylbenzene	1.0	8.4×10^{-6}	0.077	7.1	0.24	0.0024	0.0033	97	17	33	36	1.1	97
Final Headspace Volume (L) =	102	Cyclohexane	15	9.0×10^{-6}	0.088	2.3	0.003	0.0010	1.9×10^{-4}	100	46	49	53	1.1	72
Agitation Speed =	slow														
Clothes Present =	no														

13

Operating Conditions		Chemical Properties					Chemical Concentrations			Mass Transfer Parameters					
Cycle Type =	Wash	Chemical	H_c @ 23 C ($m^3 kg^{-1} m^{-3}_{gas}$)	D_1 @ 24 C (cm^2/sec)	D_g @ 24 C (cm^2/sec)	C_{lin} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,ind}$ (mg/L)	η (%)	$K_L A$ (L/min)	$k_g A$ (L/min)	k_g/k_L	Mass Closure (%)	
Duration (min) =	9.75	Acetone	0.0011	1.1×10^{-5}	0.11	31	29	0.0093	0.0073	7.0	0.011	13	10	0.74	95
Liquid Temperature (C) =	23	Toluene	0.26	9.1×10^{-6}	0.085	5.6	3.7	0.0089	0.032	33	1.5	9.6	7.1	0.74	93
Liquid Volume (L) =	49	Ethylbenzene	0.29	8.4×10^{-6}	0.077	4.9	3.0	0.0062	0.023	36	2.2	12	9.2	0.74	91
Gas Flowrate (L/min) =	53	Cyclohexane	6.7	9.0×10^{-6}	0.088	2.0	0.36	0.0061	0.025	82	9.4	11	8.4	0.74	61
Final Headspace Volume (L) =	101														
Agitation Speed =	slow														
Clothes Present =	no														

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Wash	H_2 @ 22 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,in}$	$C_{g,out}$	η	k_A	k_B	Mass Closure (%)
Duration (min) =	10	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	
Liquid Temperature (C) =	22	0.0011	1.1×10^{-5}	0.11		35	33	0.0023	0.0042	5.1	0.0084	9.3	7.5 0.81 99
Liquid Volume (L) =	47	0.24	9.1×10^{-6}	0.085		5.7	3.7	0.0019	0.016	34	2.5	15	12 0.81 79
Gas Flowrate (L/min) =	53	0.27	8.4×10^{-6}	0.077		4.8	3.1	0.0012	0.011	37	2.6	15	12 0.81 77
Final Headspace Volume (L) =	103	6.5	9.0×10^{-6}	0.088		3.3	0.78	9.4×10^{-4}	0.0094	76	9.2	11	8.8 0.81 30
Agitation Speed =	slow												
Clothes Present =	no												

14

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Wash	H_2 @ 51 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,in}$	$C_{g,out}$	η	k_A	k_B	Mass Closure (%)
Duration (min) =	10	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	
Liquid Temperature (C) =	51	0.0050	1.1×10^{-5}	0.11		45	31	0.012	0.0028	30	0.022	32	4.3 0.13 99
Liquid Volume (L) =	49	0.57	9.1×10^{-6}	0.085		8.0	2.7	0.0022	0.0096	67	3.5	49	6.6 0.13 73
Gas Flowrate (L/min) =	200	1.2	8.4×10^{-6}	0.077		7.3	2.1	0.0014	0.0067	72	4.3	31	4.2 0.13 75
Final Headspace Volume (L) =	101	16	9.0×10^{-6}	0.088		2.8	0.045	6.7×10^{-4}	0.0026	98	24	34	4.6 0.13 47
Agitation Speed =	slow												
Clothes Present =	no												

15

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Rinse	H_2 @ 21 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,in}$	$C_{g,out}$	η	k_A	k_B	Mass Closure (%)
Duration (min) =	10	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	
Liquid Temperature (C) =	21	0.0010	1.1×10^{-5}	0.11		41	33	0.011	0.021	19	0.024	2.9	24 8.6 101
Liquid Volume (L) =	50	0.24	9.1×10^{-6}	0.085		6.6	3.7	0.0089	0.036	45	0.84	1.3	11.0 8.6 92
Gas Flowrate (L/min) =	53	0.26	8.4×10^{-6}	0.077		6.1	2.6	0.0042	0.018	57	1.1	1.6	13 8.6 88
Final Headspace Volume (L) =	88	6.3	9.0×10^{-6}	0.088		2.5	0.52	0.0056	0.012	79	2.9	3.0	25 8.6 74
Agitation Speed =	slow												
Clothes Present =	yes												

16

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Rinse	H_2 @ 50 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,in}$	$C_{g,out}$	η	k_A	k_B	Mass Closure (%)
Duration (min) =	10	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	
Liquid Temperature (C) =	50	0.0048	1.1×10^{-5}	0.11		32	28	0.015	0.017	9.4	0.089	7.7	21 2.8 99
Liquid Volume (L) =	47	0.56	9.1×10^{-6}	0.085		5.9	2.6	0.0037	0.078	56	3.9	6.5	18 2.8 135
Gas Flowrate (L/min) =	200	1.1	8.4×10^{-6}	0.077		5.3	1.9	0.0035	0.051	65	4.0	5.4	15 2.8 132
Final Headspace Volume (L) =	92	16	9.0×10^{-6}	0.088		2.2	0.35	0.0058	0.0028	84	6.8	6.9	19 2.8 137
Agitation Speed =	slow												
Clothes Present =	yes												

17

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Wash	H_2 @ 18 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,in}$	$C_{g,out}$	η	k_A	k_B	Mass Closure (%)
Duration (min) =	10.5	$(m^3/m^3 \text{ gas})$	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	
Liquid Temperature (C) =	18	0.0085	1.1×10^{-5}	0.11		45	36	0.0038	0.0051	20	0.0075	5.6	9.0 1.6 104
Liquid Volume (L) =	49	0.22	9.1×10^{-6}	0.085		7.0	4.1	0.0056	0.021	42	0.58	2.2	3.6 1.6 103
Gas Flowrate (L/min) =	53	0.22	8.4×10^{-6}	0.077		5.8	2.6	0.0024	0.011	54	0.93	3.6	5.7 1.6 95
Final Headspace Volume (L) =	90	5.8	9.0×10^{-6}	0.088		2.1	0.45	0.0019	0.0099	79	3.6	4.0	6.4 1.6 78
Agitation Speed =	slow												
Clothes Present =	yes												

18

Operating Conditions	Chemical Properties			Chemical Concentrations			Mass Transfer Parameters							
	Chemical	H_c @ 49 C (m^3/m^3_{gas})	D_1 @ 24 C (cm^2/sec)	D_2 @ 24 C (cm^2/sec)	C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$ (mg/L)	η (%)	K_A (L/min)	k_gA (L/min)	Mass Closure (%)		
Wash Duration (min) = 10.5														
Liquid Temperature (C) = 49	Acetone	0.0046	1.1×10^{-5}	0.11	47	37	0.020	0.012	22	0.082	5.9	18	3.1	99
Liquid Volume (L) = 49	Toluene	0.54	9.1×10^{-6}	0.085	6.7	2.6	0.0078	0.023	62	2.1	3.4	11	3.1	100
Gas Flowrate (L/min) = 200	Ethylbenzene	1.1	8.4×10^{-6}	0.077	5.5	1.7	0.0043	0.015	69	2.2	2.9	8.9	3.1	96
Final Headspace Volume (L) = 90	Cyclohexane	15	9.0×10^{-6}	0.088	1.8	0.12	0.0020	0.0094	94	6.0	6.2	19	3.1	131
Agitation Speed = slow														
Clothes Present = yes														

19

Operating Conditions	Chemical Properties			Chemical Concentrations			Mass Transfer Parameters						
	H_c @ 21 C (m^3/m^3)	D_1 @ 24 C (cm^2/sec)	D_2 @ 24 C (cm^2/sec)	C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,end}$	η (%)	K_A (L/min)	k_gA (L/min)	Mass Closure (%)		
Rinse Duration (min) = 9.75													
Liquid Temperature (C) = 21	0.0010	1.1×10^{-5}	0.11	19	18	0.0087	0.0063	3.4	0.024	6.4	24	3.7	100
Liquid Volume (L) = 82	0.0042	9.5×10^{-6}	0.092	13	13	0.0056	0.010	5.2	0.053	3.4	12	3.7	102
Gas Flowrate (L/min) = 53	0.24	9.1×10^{-6}	0.085	3.2	2.4	0.0022	0.014	26	2.7	5.6	21	3.7	88
Final Headspace Volume (L) = 58	0.3	8.4×10^{-6}	0.077	3.0	2.1	0.0016	0.0091	28	3.0	6.1	23	3.7	85
Agitation Speed = slow	6.5	9.0×10^{-6}	0.088	1.5	1.0	6.6×10^{-4}	0.0053	36	3.4	3.6	13	3.7	81
Clothes Present = no													

20

Operating Conditions		Chemical Properties			Chemical Concentrations				Mass Transfer Parameters					
Cycle Type =	Rinse	H _c @ 21 C (m ³ /m ³ gas)	D ₁ @ 24 C (cm ² /sec)	D ₂ @ 24 C (cm ² /sec)	C _{in}	C _{out}	C _{g,in}	C _{g,prod}	η (%)	K _A (L/min)	k _g A (L/min)	Mass Closure (%)		
Duration (min) =	10	0.0010	1.1 × 10 ⁻⁵	0.11	38	36	0.010	0.010	4.8	0.020	9.7	20	2.1	98
Liquid Temperature (C) =	21	0.0010	1.1 × 10 ⁻⁵	0.11	38	36	0.010	0.010	4.8	0.020	9.7	20	2.1	98
Liquid Volume (L) =	95	0.0042	9.5 × 10 ⁻⁶	0.092	27	25	0.0072	0.016	5.2	0.039	4.6	9.5	2.1	100
Gas Flowrate (L/min) =	53	0.24	9.1 × 10 ⁻⁶	0.085	6.5	4.8	0.0031	0.027	28	2.9	8.8	18	2.1	82
Final Headspace Volume (L) =	55	0.3	8.4 × 10 ⁻⁶	0.077	6.2	4.8	0.0022	0.019	31	3.2	9.1	19	2.1	83
Agitation Speed =	slow	6.4	9.0 × 10 ⁻⁶	0.088	2.6	1.4	0.0014	0.0096	44	5.2	5.6	12	2.1	73
Clothes Present =	no													

21

Operating Conditions		Chemical Properties			Chemical Concentrations			Mass Transfer Parameters						
Cycle Type =	Rinse	H _c @ 51°C (m ³ /m ³ gas)	D ₁ @ 24°C (cm ² /sec)	D _g @ 24°C (cm ² /sec)	C _{lin}	C _{foot}	C _{gin}	C _{gend}	η (%)	K _A (L/min)	k _g A (L/min)	Mass Closure (%)		
Duration (min) =	10													
Liquid Temperature (C) =	51	0.0050	1.1 x 10 ⁻⁵	0.11	39	37	0.021	0.020	3.1	0.15	6.0	30	5.1	99
Liquid Volume (L) =	96	0.015	9.5 x 10 ⁻⁶	0.092	19	18	0.014	0.018	5.1	0.25	3.5	18	5.1	101
Gas Flowrate (L/min) =	200	0.56	9.1 x 10 ⁻⁶	0.085	6.5	4.8	0.0039	0.0068	33	3.3	4.4	23	5.1	86
Final Headspace Volume (L) =	54	1.1	8.4 x 10 ⁻⁶	0.077	5.7	4.0	0.0027	0.0053	32	2.9	3.4	17	5.1	87
Agitation Speed =	slow	16	9.0 x 10 ⁻⁶	0.088	2.0	1.1	8.6 x 10 ⁻⁴	0.0026	44	4.5	4.5	23	5.1	79
Clothes Present =	no													

22

Operating Conditions			Chemical Properties			Chemical Concentrations			Mass Transfer Parameters				
Cycle Type =	H_c @ 48 C (m^3/m^3)	D_1 @ 24 C (cm^2/sec)	D_2 @ 24 C (cm^2/sec)	C_{in} (mg/L)	C_{out} (mg/L)	$C_{g,in}$ (mg/L)	$C_{g,ind}$ (mg/L)	η (%)	K_A (L/min)	k_gA (L/min)	k_g/k_L	Mass Closure (%)	
Rinse	Chemical												
Duration (min) =	0.00095	1.1×10^{-5}	0.11	39	33	0.014	0.018	16	0.048	99	49	0.50	
10	0.0040	9.5×10^{-6}	0.092	27	23	0.011	0.093	16	0.091	45	22	0.50	
20	0.24	9.1×10^{-6}	0.085	6.7	2.0	0.0034	0.079	70	11	103	51	0.50	
Liquid Temperature (C) =	0.3	8.4×10^{-6}	0.077	5.9	1.5	0.0033	0.062	74	12	110	55	0.50	
48	6.3	9.0×10^{-6}	0.088	2.0	0.0	0.0055	0.0029	100	52	68	34	0.50	
Liquid Volume (L) =													
53													
Gas Flowrate (L/min) =													
102													
Final Headspace Volume (L) =													
fast													
Agitation Speed =													
no													

23

24

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Cycle Type =	Rinse	H_c @ 49 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,nd}$	η	K_A	k_A	k_g/k_i Mass Closure
Duration (min) =	10.25	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	49	0.0046	1.1×10^{-5}	0.11		42	29	0.014	31	0.31	120	69 0.58 97
Liquid Volume (L) =	49	0.014	9.5×10^{-6}	0.092		18	12	0.0081	34	0.82	103	59 0.58 112
Gas Flowrate (L/min) =	200	0.53	9.1×10^{-6}	0.085		7.4	0.070	0.0017	99	38	161	92 0.58 68
Final Headspace Volume (L) =	101	1.0	8.4×10^{-6}	0.077		6.8	0.054	0.0013	99	38	101	58 0.58 57
Agitation Speed =	fast	15	9.0×10^{-6}	0.088		2.7	0.0038	7.6×10^{-4}	100	94	105	61 0.58 92
Clothes Present =	no											

25

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Cycle Type =	Rinse	H_c @ 18 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,nd}$	η	K_A	k_A	k_g/k_i Mass Closure
Duration (min) =	10	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	18	0.0085	1.1×10^{-5}	0.11		42	37	0.0036	10	0.023	3.9	11 2.8 99
Liquid Volume (L) =	95	0.0037	9.5×10^{-6}	0.092		26	24	0.0044	7.8	0.055	3.2	8.9 2.8 103
Gas Flowrate (L/min) =	53	0.22	9.1×10^{-6}	0.085		6.1	4.7	0.0057	24	1.5	3.8	11 2.8 93
Final Headspace Volume (L) =	55	0.2	8.4×10^{-6}	0.077		5.0	3.8	0.0039	24	1.5	4.0	11 2.8 92
Agitation Speed =	fast	5.8	9.0×10^{-6}	0.088		1.9	1.2	0.0032	48	2.9	3.1	8.7 2.8 85
Clothes Present =	no											

26

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Cycle Type =	Rinse	H_c @ 50 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,nd}$	η	K_A	k_A	k_g/k_i Mass Closure
Duration (min) =	10	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	50	0.0048	1.1×10^{-5}	0.11		45	39	0.015	15	0.086	9.0	9.0 1.0 102
Liquid Volume (L) =	94	0.015	9.5×10^{-6}	0.092		23	18	0.011	22	0.13	3.8	3.8 1.0 98
Gas Flowrate (L/min) =	200	0.56	9.1×10^{-6}	0.085		6.4	4.3	0.0026	33	1.5	4.3	4.3 1.0 105
Final Headspace Volume (L) =	56	1.1	8.4×10^{-6}	0.077		5.1	3.3	0.0017	34	1.7	3.2	3.2 1.0 101
Agitation Speed =	fast	16	9.0×10^{-6}	0.088		1.7	0.84	5.4×10^{-4}	62	5.9	6.3	6.3 1.0 90
Clothes Present =	no											

STUDY:

Shepherd, Kemp, and Corsi

1996

Reference: *Journal of the Air and Waste Management Association*, Vol. 46, No. 7, 1996, pp. 631-642.

Solution Method:

Method 8. Stripping efficiencies based on predicted $C_{g,nd}$ values using K_A values.

Assumptions:

 $C_{g,nd} = C_g = 0$.Comments: K_A values are equal to the total liquid volume multiplied by the K_A values reported in the paper, where a equals AN_L .

* = Could not be determined with available data.

27

Operating Conditions		Chemical Properties				Chemical Concentrations			Mass Transfer Parameters			
Cycle Type =	Rinse	H_c @ 31 C	D_1 @ 24 C	D_2 @ 24 C	D_3 @ 24 C	C_{in}	C_{out}	$C_{g,nd}$	η	K_A	k_A	k_g/k_i Mass Closure
Duration (min) =	10	(m^3/m^3)	(cm^2/sec)	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	31	0.24	9.7×10^{-6}	0.10		1.0	0.50	0	50	5.2	*	*
Liquid Volume (L) =	74											
Gas Flowrate (L/min) =	180											
Final Headspace Volume (L) =	55											
Mass of Clothes Present (kg) =	0											

Operating Conditions		Chemical Properties		Chemical Concentrations		Mass Transfer Parameters				
Cycle Type =		$H_c @ 31\text{ C}$ $D_i @ 24\text{ C}$ $D_o @ 24\text{ C}$		$C_{i,in}$	$C_{i,out}$	$C_{g,in}$	$C_{g,end}$	η	K_A	k_A
Duration (min) =		(m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)
Liquid Temperature (C) =		31		1.0	0.82	0	0	18	1.5	*
Liquid Volume (L) =		74								*
Gas Flowrate (L/min) =		180								*
Final Headspace Volume (L) =		55								*
Mass of Clothes Present (kg) =		4.5								*

Operating Conditions		Chemical Properties		Chemical Concentrations		Mass Transfer Parameters				
Cycle Type =		$H_c @ 32\text{ C}$ $D_i @ 24\text{ C}$ $D_o @ 24\text{ C}$		$C_{i,in}$	$C_{i,out}$	$C_{g,in}$	$C_{g,end}$	η	K_A	k_A
Duration (min) =		(m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)
Liquid Temperature (C) =		32		1.0	0.76	0	0	24	2.1	*
Liquid Volume (L) =		74								*
Gas Flowrate (L/min) =		180								*
Final Headspace Volume (L) =		55								*
Mass of Clothes Present (kg) =		0								*

Operating Conditions		Chemical Properties		Chemical Concentrations		Mass Transfer Parameters				
Cycle Type =		$H_c @ 33\text{ C}$ $D_i @ 24\text{ C}$ $D_o @ 24\text{ C}$		$C_{i,in}$	$C_{i,out}$	$C_{g,in}$	$C_{g,end}$	η	K_A	k_A
Duration (min) =		(m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)
Liquid Temperature (C) =		33		1.0	0.88	0	0	12	2.1	*
Liquid Volume (L) =		74								*
Gas Flowrate (L/min) =		180								*
Final Headspace Volume (L) =		55								*
Mass of Clothes Present (kg) =		0								*

Operating Conditions		Chemical Properties		Chemical Concentrations		Mass Transfer Parameters				
Cycle Type =		$H_c @ 31\text{ C}$ $D_i @ 24\text{ C}$ $D_o @ 24\text{ C}$		$C_{i,in}$	$C_{i,out}$	$C_{g,in}$	$C_{g,end}$	η	K_A	k_A
Duration (min) =		(m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)
Liquid Temperature (C) =		31		1.0	0.90	0	0	9.5	0.96	*
Liquid Volume (L) =		74								*
Gas Flowrate (L/min) =		180								*
Final Headspace Volume (L) =		55								*
Mass of Clothes Present (kg) =		2.3								*

Operating Conditions		Chemical Properties		Chemical Concentrations		Mass Transfer Parameters				
Cycle Type =		$H_c @ 31\text{ C}$ $D_i @ 24\text{ C}$ $D_o @ 24\text{ C}$		$C_{i,in}$	$C_{i,out}$	$C_{g,in}$	$C_{g,end}$	η	K_A	k_A
Duration (min) =		(m^3/m^3_{gas}) (cm^2/sec) (cm^2/sec)		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)
Liquid Temperature (C) =		31		1.0	0.75	0	0	25	1.5	*
Liquid Volume (L) =		74								*
Gas Flowrate (L/min) =		180								*
Final Headspace Volume (L) =		55								*
Mass of Clothes Present (kg) =		2.3								*

33														
Operating Conditions			Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Wash		H_b @ 29 C	D_l @ 24 C	D_g @ 24 C	C_{lin}	C_{liot}	C_{gin}	C_{gend}	η	K_dA	k_dA	k_gA	Mass Closure
Duration (min) =	10	Chemical	(m^3_{mol}/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	29	Chloroform	0.21	9.7×10^{-6}	0.10	1.0	0.82	0	0	18	0.74	*	*	*
Liquid Volume (L) =	74													
Gas Flowrate (L/min) =	180													
Final Headspace Volume (L) =	55													
Mass of Clothes Present (kg) =	4.5													

34														
Operating Conditions		Chemical Properties			Chemical Concentrations				Mass Transfer Parameters					
Cycle Type =	Wash													
Duration (min) =	10													
Liquid Temperature (C) =	30													
Liquid Volume (L) =	74													
Gas Flowrate (L/min) =	180													
Final Headspace Volume (L) =	55													
Mass of Clothes Present (kg) =	4.5													
		H ₂ @ 30 C	D _l @ 24 C	D _g @ 24 C	C _{lin}	C _{liot}	C _{gin}	C _{gend}	η	K _{dA}	k _{dA}	k _{gA}	k _{g/k}	Mass Closure
		(m ³ /m ³ _{gas})	(cm ² /sec)	(cm ² /sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(L/min)	(L/min)	(%)
		Chemical	0.22	9.7 x 10 ⁻⁶	0.10	1.0	0.83	0	0	17	1.4	*	*	*
		Chloroform												

STUDY: Wooley, Nazaroif, and Hodgson
Study year: 1990
Reference: *Journal of the Air and Waste Management Association*, Vol. 40, 1990, pp. 1114-1120
Solution Method: Not enough information given to solve K_{dA} .
 Stripping efficiency values based on mass of ethanol added to wash water and mass of ethanol remaining after operation.
Assumptions: $C_{gin} = 0$,
 Mass closure values from paper.
Comments: * = Could not be determined with available data.

Operating Conditions		Chemical Properties			Chemical Concentrations		Mass Transfer Parameters				
Cycle Type =	wash	H_b @ 35 C	D_l @ 24 C	D_g @ 24 C	Initial Mass	Final Mass	η	K_{dA}	k_dA	k_{dA}	Mass Closure
Duration (min) =	9	Chemical	(m^3/m^3_{gas})	(cm^2/sec)	(g)	(g)	(%)	(L/min)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	35	Ethanol	7.3×10^{-4}	1.3×10^{-5}	0.12	9.7	8.7	10	*	*	90
Liquid Volume (L) =	*	Ethanol	7.3×10^{-4}	1.3×10^{-5}	0.12	9.6	8.6	10	*	*	90
Gas Flowrate (L/min) =	*	Ethanol	7.3×10^{-4}	1.3×10^{-5}	0.12	9.7	9.1	6.2	*	*	93
Final Headspace Volume (L) =	*										
Mass of Clothes Present (kg) =	3.1										

Operating Conditions		Chemical Properties			Chemical Concentrations		Mass Transfer Parameters					
Cycle Type =	wash	H_c @ 55 C	D_l @ 24 C	D_g @ 24 C	Initial Mass	Final Mass	η	k_{dA}	k_A	k_{dA}	k_A/k_d	Mass Closure
Duration (min) =	9	Chemical	(m^3/m^3_{gas})	(cm^2/sec)	(g)	(g)	(%)	(μ min)	(μ min)	(μ min)		(%)
Liquid Temperature (C) =	55	Ethanol	1.3×10^{-5}	0.12	10	8.7	13	*	*	*	*	89
Liquid Volume (L) =	*	Ethanol	1.3×10^{-5}	0.12	9.8	9.4	4.1	*	*	*	*	97
Gas Flowrate (μ min) =	*	*	1.3×10^{-5}	0.12	9.7	9.1	6.2	*	*	*	*	95
Final Headspace Volume (L) =	*	Ethanol										
Mass of Clothes Present (kg) =	3.1											

A-45

DISHWASHER DATABASE

- initial lipid-phase concentration based on average of duplicate samples with a relative difference greater than 20%, but no more than 36%.

ned with available data.

Entry #

[illegible]

2

[illegible]

မိ

[illegible]

4

[illegible]

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Wash	H_e @ 45 C	D_i @ 24 C	D_o @ 24 C		C_{in}	C_{out}	C_{in}	C_{out}	η	K_A	k_A	k_d/k_i Mass Closure
Duration (min) =	10	Chemical	(m^3_{liq}/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	45	Acetone	0.0037	1.1×10^{-5}	0.11	61	32	0.014	0.34	47	6.8	*	83
Liquid Volume (L) =	7.4	Toluene	0.49	9.1×10^{-6}	0.085	12	0.41	0.005	0.31	98	33	*	95
Headspace Volume (L) =	181	Ethylbenzene	0.90	8.4×10^{-6}	0.077	12	0.29	0.004	0.23	98	35	*	90
Ventilation Rate (L/min) =	5.7	Cyclohexane	14	9.0×10^{-6}	0.088	6.4	0.016	0.002	0.10	100	50	*	88
Dishes Present =	Yes												

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Wash	H_e @ 38 C	D_i @ 24 C	D_o @ 24 C		C_{in}	C_{out}	C_{in}	C_{out}	η	K_A	k_A	k_d/k_i Mass Closure
Duration (min) =	10	Chemical	(m^3_{liq}/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	38	Acetone	0.0026	1.1×10^{-5}	0.11	61	36	0	0.23	42	9.4	*	94
Liquid Volume (L) =	7.4	Toluene	0.40	9.1×10^{-6}	0.085	14	0.58	0	0.29	96	34	*	92
Headspace Volume (L) =	181	Ethylbenzene	0.64	8.4×10^{-6}	0.077	14	0.41	0	0.21	97	36	*	87
Ventilation Rate (L/min) =	5.7	Cyclohexane	11	9.0×10^{-6}	0.088	9.2	0.022	0	0.088	100	62	62	83
Dishes Present =	Yes												

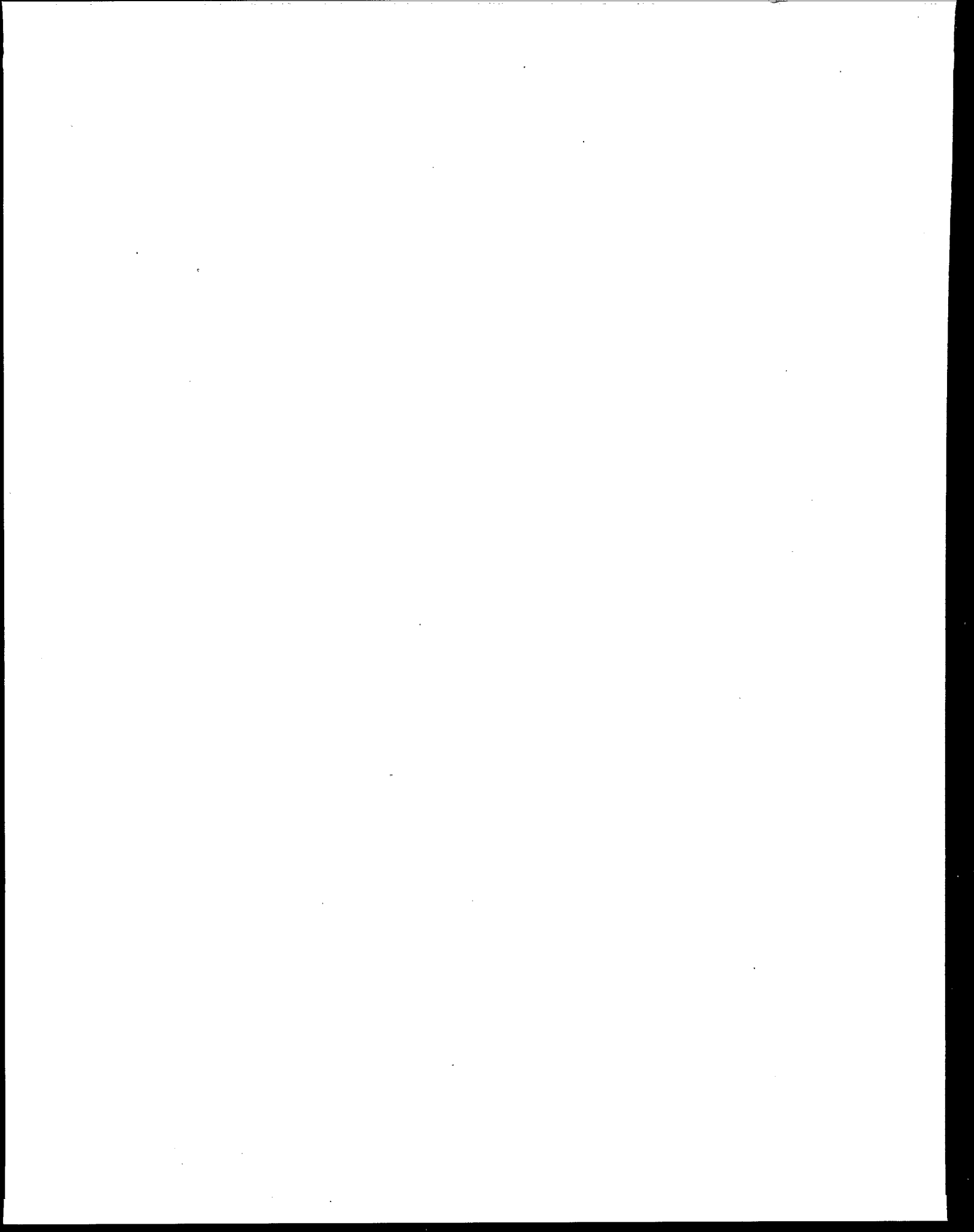
Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Rinse	H_e @ 55 C	D_i @ 24 C	D_o @ 24 C		C_{in}	C_{out}	C_{in}	C_{out}	η	K_A	k_A	k_d/k_i Mass Closure
Duration (min) =	7	Chemical	(m^3_{liq}/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	55	Acetone	0.0081	1.1×10^{-5}	0.11	97	44	0	0.47	55	8.2	*	90
Liquid Volume (L) =	7.4	Toluene	0.62	9.1×10^{-6}	0.085	16	0.36	0	0.33	98	39	*	92
Headspace Volume (L) =	181	Ethylbenzene	1.3	8.4×10^{-6}	0.077	15	0.24	0	0.24	98	42	*	87
Ventilation Rate (L/min) =	5.7	Cyclohexane	18	9.0×10^{-6}	0.088	7.0	0.011	0	0.094	100	57	56	86
Dishes Present =	No												

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Rinse	H_e @ 55 C	D_i @ 24 C	D_o @ 24 C		C_{in}	C_{out}	C_{in}	C_{out}	η	K_A	k_A	k_d/k_i Mass Closure
Duration (min) =	6.75	Chemical	(m^3_{liq}/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	55	Acetone	0.0061	1.1×10^{-5}	0.11	58	48	0	0.33	18	1.7	*	100
Liquid Volume (L) =	7.4	Toluene	0.62	9.1×10^{-6}	0.085	13	0.46	0	0.24	96	33	*	91
Headspace Volume (L) =	181	Ethylbenzene	1.4	8.4×10^{-6}	0.077	15	0.37	0	0.18	97	36	*	83
Ventilation Rate (L/min) =	5.7	Cyclohexane	18	9.0×10^{-6}	0.088	9.2	0.019	0	0.080	100	56	50	81
Dishes Present =	Yes												

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters			
Cycle Type =	Wash	H_e @ 54 C	D_i @ 24 C	D_o @ 24 C		C_{in}	C_{out}	C_{in}	C_{out}	η	K_A	k_A	k_d/k_i Mass Closure
Duration (min) =	7	Chemical	(m^3_{liq}/m^3_{gas})	(cm^2/sec)	(cm^2/sec)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(%)	(L/min)	(L/min)	(%)
Liquid Temperature (C) =	54	Acetone	0.0058	1.1×10^{-5}	0.11	62	30	0	0.44	51	7.6	*	94
Liquid Volume (L) =	7.4	Toluene	0.61	9.1×10^{-6}	0.085	16	0.38	0	0.30	98	38	*	97
Headspace Volume (L) =	181	Ethylbenzene	1.3	8.4×10^{-6}	0.077	17	0.28	0	0.22	98	41	*	92
Ventilation Rate (L/min) =	5.7	Cyclohexane	18	9.0×10^{-6}	0.088	7.9	0.015	0	0.083	100	50	50	92
Dishes Present =	No												

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters				
Cycle Type =	Wash	$H_o @ 55\text{ C}$ $D_l @ 24\text{ C}$ $D_g @ 24\text{ C}$				$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,end}$	η	$K_L A$	k_A	k_{gA}	k_g/k_l Mass Closure (%)
Duration (min) =	6.67	Chemical (m^3_{liq}/m^3_{gas}) (cm^2/sec) (cm^2/sec)				(mg/L) (mg/L) (mg/L) (mg/L)				$(\%)$ (L/min) (L/min) (L/min) $(\%)$				
Liquid Temperature (C) =	55	Acetone	0.0061	1.1×10^{-5}	0.11	44	28	0.052	0.48	37	4.9	*	*	100
Liquid Volume (L) =	7.4	Toluene	0.62	9.1×10^{-6}	0.085	9.9	0.34	0.010	0.29	97	31	*	*	98
Headspace Volume (L) =	181	Ethylbenzene	1.4	8.4×10^{-6}	0.077	10	0.25	0.008	0.21	97	34	*	*	90
Ventilation Rate (L/min) =	5.7	Cyclohexane	18	9.0×10^{-6}	0.088	5.1	0.014	0.004	0.080	100	47	46	*	85
Dishes Present =	Yes													

Operating Conditions		Chemical Properties				Chemical Concentrations				Mass Transfer Parameters				
Cycle Type =	Wash	$H_o @ 53\text{ C}$ $D_l @ 24\text{ C}$ $D_g @ 24\text{ C}$				$C_{l,in}$	$C_{l,out}$	$C_{g,in}$	$C_{g,end}$	η	$K_L A$	k_A	k_{gA}	k_g/k_l Mass Closure (%)
Duration (min) =	6.67	Chemical (m^3_{liq}/m^3_{gas}) (cm^2/sec) (cm^2/sec)				(mg/L) (mg/L) (mg/L) (mg/L)				$(\%)$ (L/min) (L/min) (L/min) $(\%)$				
Liquid Temperature (C) =	53	Acetone	0.0066	1.1×10^{-5}	0.11	60	36	0.008	0.48	40 [#]	5.2	*	*	97
Liquid Volume (L) =	7.4	Toluene	0.6	9.1×10^{-6}	0.085	15	0.48	0.003	0.26	97 [#]	35	*	*	88
Headspace Volume (L) =	181	Ethylbenzene	1.3	8.4×10^{-6}	0.077	17	0.41	0.0020	0.19	98 [#]	37	*	*	82
Ventilation Rate (L/min) =	5.7	Cyclohexane	17	9.0×10^{-6}	0.088	8.5	0.026	0	0.092	100 [#]	55	54	*	84
Dishes Present =	Yes													



United States
Environmental Protection Agency/ORD
National Center for
Environmental Assessment
Washington, D.C. 20460

Official Business
Penalty for Private Use
\$300
EPA/600/R-00/096

Please make all necessary changes on the below label,
detach or copy, and return to the address in the upper
left-hand corner.
If you do not wish to receive these reports CHECK HERE ☐ :
detach, or copy this cover, and return to the address in the
upper left-hand corner.